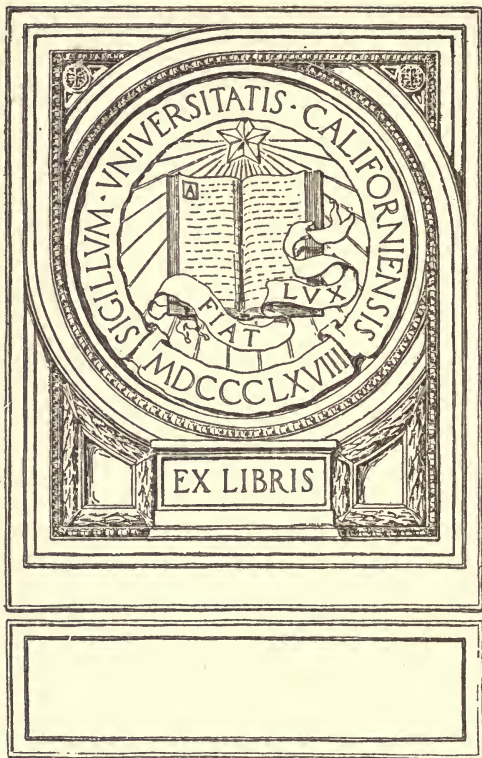




• ESSENTIALS OF CHEMISTRY •

BY

hewson

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INSTRUCTOR IN CHEMISTRY, THE ENGLEWOOD HIGH SCHOOL,
CHICAGO

REVISED EDITION (1912)

BY

JOHN C. HESSLER

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P R E F A C E.

The Revised Edition of the " Essentials of Chemistry " retains the scientific character of the original text, but the method of treatment and the order of topics have been modified in accordance with the experience of the past ten years. These years have brought about significant changes in the Chemistry courses of secondary schools. Not only has the number of students increased greatly, but chemical science has become more and more important as a prerequisite for work in the other sciences and in applied courses. In view of this increased and altered demand for chemical instruction, authors are tempted to neglect the basic principles of the science, and to enlarge upon the purely descriptive matter. But Chemistry that is merely descriptive is not an adequate preparation even for applied courses. What is sought of Chemistry, both by those who study it as a prerequisite for other work, and by those whose sole aim is general culture, is, **essentially**, the *chemical point of view*. To present that point of view properly, a text-book must include a correct, even if simple, treatment of chemical theory. Especially

must it include recent physico-chemical conceptions, such as *equilibrium*, that have a general application to both physical and chemical changes.

The revision of the "Essentials" has been made with the purpose of meeting these demands. The most important changes and additions are the following:—

1. The **theoretical matter** has been presented **earlier** than in the original edition, and it has been broken up into portions more suitable for study and assimilation. Chapter I contains, besides the specifically chemical topics of changes, elements, etc., a short account of matter, energy, mass, and density. The idea that energy is associated with matter in *substances* is brought out in Chapter II, that on Oxygen. The gas laws are given in Chapter III. Problems on the relation of volume to temperature and pressure are solved by the fractional method rather than by the method of proportions. The laws of definite proportions and of equivalent weights are given in the chapter on Water (V). The law of multiple proportions and the atomic and molecular hypotheses appear in Chapter VII. Chapter VIII treats of equations and of calculations from formulas and equations. The methods for determining molecular weights are given in Chapter XII; those for atomic weights, in Chapter XIII. Molecular formulas and equations, constitutional formulas, and isomers are topics of Chapter XVIII.

2. The treatment of **Valence**, which took only a part of a chapter in the first edition, makes up Chapter XI of the revised book. A valence table of the common elements and radicals is given, and the application of valence to the construction of formulas receives special attention.

3. **Equilibrium**, like valence, has been given a separate chapter. The notions of *physical* equilibrium, as applied to changes of state and to solution, precede the discussion of chemical and ionic equilibrium.

4. The influence of the several factors in solution and crystallization is brought out in Chapter VI, and several solubility curves are given. A quantitative table of solubility for many common compounds is inserted in the Appendix.

5. The chapter on Acids, Bases, and Salts (XIV) contains a section on **equivalent** (normal) **solutions**. The theory of ionization and electrolysis is given in Chapter XV.

6. The "**nascent state**" is ascribed, not to the atomic state of the nascent element, but to the presence of catalyzers or excessive amounts of energy.

7. The new book is especially strong in its **industrial** features. The following facts illustrate this:—

a. The methods of purifying and softening water are given in detail.

b. The commercial methods of making hydrochloric and nitric acids receive adequate attention and special illustrations, as does the "contact process" for sulphuric acid.

c. The applications of the electric furnace and modern electrolytic processes are carefully considered.

d. The description of the copper, iron, and steel manufacture is detailed and thoroughly modern.

e. Mordants and dyes are treated in a fundamental way.

8. The new book shows that the properties of the sulphides form the basis of the **Qualitative Analysis** of the metals, and the Qualitative grouping is compared with the Periodic Arrangement.

9. The **Exercises** of the revised text are largely new, and more numerous than in the original edition.

10. *The new book has 92 illustrations, as compared with 65 in the older edition. All but 10 of these are from new drawings. Every page of the book has been reset.*

The reviser wishes to express his thanks to Dr. Oliver C. Farrington, of the Field Museum of Natural History, Chicago, for the photograph of White's Cave (Fig. 64); to the J. T. Baker Chemical Company, publishers of *The Chemist-Analyst*, for the illustrations of the hydrochloric acid and nitric acid manufacture (Figs. 32 and 50); and to the United Gas Improvement Company, Philadelphia, for the cut illustrating the making of "water gas" (Fig. 68).

About half of the drawings for the new illustrations were made by Miss Margaret C. Hessler. The remainder are the work of Mr. Corry Wilkin, Mr. Barton Westervelt, Mr. Andrew Bolay, and Mr. Claude Postlewait. To all of these the reviser expresses his thanks. He is also greatly indebted, and correspondingly grateful, to his colleague, Dr. Eugene C. Woodruff, of the James Millikin University, and to Mr. Leslie A. Touzalin, of the Illinois Steel Works, Chicago, for many helpful suggestions given during the preparation of this revision.

J. C. H.

JUNE, 1912.

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CHEMISTRY.

CHAPTER I.

INTRODUCTION.

1. **Substances and Properties.** — Chemistry may be defined as the science that deals with *substances and the changes they undergo*. We distinguish between substances by their *characteristics*, or qualities. Thus, a diamond has greater *hardness*, or scratching power, than glass, and a silver coin gives a distinct “ring” when thrown upon a table, while a lead coin falls with a “thud.” The characteristics of substances are called **properties**. Among the properties of a substance are its odor, taste, color, melting temperature, boiling temperature, ability or inability to dissolve, burn, etc.

2. **Changes in Substances.** — The changes that substances undergo may be the so-called **natural** changes, such as the freezing of water, the fermenting of fruit juices, and the rusting of iron, or they may be brought about by man, such as the extraction of lead from its ore, the magnetizing of iron, the dis-

tillation of water, and the burning of coal. In every one of these cases we know that there has been a change because some of the **properties** of the substance obtained are **different** from those of the substance taken. The boiled water is changed to a colorless, light vapor — steam; the magnetized iron can attract other objects of iron or steel; the fermented fruit juice contains new substances, e. g., *alcohol*, *acetic acid*, etc., not present before fermentation.

3. Physical and Chemical Changes. — The changes given in § 2 (and all others) may be divided into two classes:

(1) Physical changes.

(2) Chemical changes.

To the *first* class belong those changes in which the substance is **not permanently altered**, but regains its original properties after the change. A physical change may usually be repeated with the same substance. Illustrations are: the magnetization of a knife blade, the production of light by the incandescence of carbon (electric light), the melting of ice, and the boiling away of water.

Chemical changes, on the other hand, involve a **permanent** alteration in the substance. Thus, *burnt* magnesium does not revert to magnesium when cooled; rusted iron has lost the properties of iron; the carbon dioxide produced when coal is burned is

neither carbon nor oxygen, although these substances united to produce it.

4. Physical and Chemical Properties. — Just as we divide *changes* into physical and chemical changes, so we classify the **properties** of substances as either *physical* or *chemical* properties. Those properties are *physical* that can be determined *without a chemical change*. Such are the boiling temperature, melting temperature, specific gravity, taste, odor, etc. *Chemical* properties can be shown *only by a chemical change*. The combustibility of sulphur is shown by burning it — a chemical change.

When a substance is described in Chemistry, its most important physical as well as chemical properties are given. In fact, our most common method of telling that a chemical change has taken place is to note the changes in the physical properties of the substances used. Thus, when *mercuric chloride* and *potassium iodide*, two **white** solids, are ground together in a mortar, a bright **scarlet** powder is obtained. The change of color, alone, suggests that some new substance has been formed.

5. Reagents and Reactions. — Substances which have a chemical effect upon one another are said to *react*, and a chemical change is therefore called a *reaction*. The substances which react are called *reagents*, or *factors*. The substances formed are the

products. Thus, when copper is treated with concentrated nitric acid, a *chemical reaction* takes place, and the copper and the nitric acid are the *reagents* (or factors). The brown gas formed is one of several products.

The adjective "reagent" is often applied to substances in the form in which they are commonly used in the laboratory. Thus "reagent" ammonia means an *aqueous solution* of ammonia; ammonia itself is a gas. Similarly, by "reagent" sodium hydroxide we mean the solution of solid sodium hydroxide in water.

6. Matter and Energy.

Substances are the *kinds of matter* (cf. § 1). **Matter** itself may be defined as that which **occupies space**, or *takes up room*. Matter also has **weight**, that is, *it attracts other matter*. The earth's attraction for matter at or near its surface is called *gravity*.

The **mass** of a body is the *quantity of matter* in it. At a given place, the mass of a body is measured by its weight. The *weight may change* as the earth's attraction for the body changes. Thus, bodies weigh most at the earth's surface and at its poles. The *mass*, of course, *remains the same everywhere*.

The **density** of a substance is the *mass of it in unit volume*. Thus, 1 c.c. (cf. Appendix i) of iron weighs 7.8 grams; iron has, therefore, a density of 7.8.

The **specific gravity**, or *relative density*, of a substance is obtained by dividing the weight of a given volume of the substance by the weight of the same volume of some standard substance. For liquids and solids the standard is pure water at 4° C. (cf. § 71).

$$\text{Specific Gravity} = \frac{\text{Weight of body}}{\text{Weight of equal volume of water}}.$$

For gases the standard is air or hydrogen (*cf.* § 51).

Energy. — A third property of matter is *inertia*, or *helplessness*. Matter cannot move itself if at rest, nor stop itself if moving, nor change the velocity or direction of its motion. Anything that can produce changes in the motion of matter is called a **force**. Gravity, steam, and the wind are forces. Matter under the influence of a force can do **work** upon other matter, and is said to “possess **energy**.” Thus, falling water drives a mill-wheel; it has *energy*. The wind — air in motion — drives a windmill or a ship. Steam engines run because of the expansion — motion — of steam. These are all examples of *physical* forces. Coal also possesses energy — **chemical energy**. When it burns (a chemical change) heat is liberated, and this heat can generate steam to run an engine or a dynamo (*cf.* § 27).

7. Physical States of Matter. — Matter may exist in the *solid*, *liquid*, and *gaseous* condition. Thus, water is known as *ice*, *liquid water*, and *steam*. The air is commonly a gas, but it may be liquefied and even frozen (*cf.* § 197). The same is true of other gases.

In the solid state a substance has a *definite form*, but this is not true of liquids and gases. Liquids have definite volumes, but they take their form from the vessel holding them. Gaseous bodies are without form or volume of their own. When they are put into a vessel they spread in all directions and fill it completely. Although changes of physical state are accompanied by decided alterations of proper-

ties, they are called *physical* changes and not chemical changes; we can reverse them by restoring the original conditions.

8. Elements and Compounds. — Almost all substances may be shown to consist of two or more different substances, and are therefore called **compound substances**, or *compounds*. There are, however, between seventy and eighty substances which we are unable to decompose, *with our present methods*; these are called **elements**. The thousands of compounds known are made up of this relatively small number of elements. Less than half of the elements are ever found *free* in nature; the others occur only as parts of compounds, and must be separated from combination by chemical processes. A list of the elements is given in Appendix iii.

Two Classes of Elements. — The elements are generally divided into two classes: **metals** and **non-metals**. There are important *physical* differences between the two classes. Thus, the metals have a peculiar luster, they are malleable, ductile, etc., while the non-metals lack these properties. All metals are solids under ordinary conditions except mercury. Some of the non-metals are solids, like phosphorus and sulphur, or gases, like oxygen and chlorine. Bromine is a liquid. The *chemical* differences are also very important (*cf.* § 161).

9. Abundance of the Elements.

Not half of the elements are at all common; many are very rare. F. W. Clarke has made an estimate of their abundance (see following table). The solid crust is assumed to make up 93% of the earth; the ocean, about 7%, and the atmosphere, 0.03%.

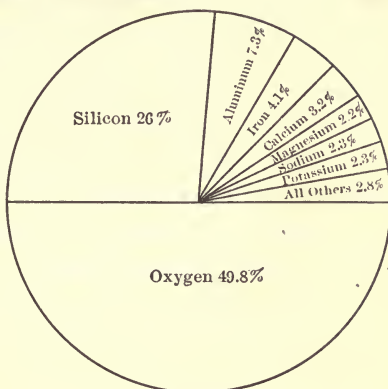


FIG. 1.

ELEMENT.	PER CENT OF SOLID CRUST.	PER CENT OF OCEAN.	AVERAGE, INCLUD- ING ATMOSPHERE.
Oxygen.	47.07	85.79	49.78
Silicon.	28.06		26.08
Aluminum.	7.90		7.34
Iron.	4.43		4.11
Calcium.	3.44	0.05	3.19
Magnesium.	2.40	0.14	2.24
Sodium.	2.43	1.14	2.33
Potassium.	2.45	0.04	2.28
Hydrogen.	0.22	10.67	0.95
Titanium.	0.40		0.37
Carbon.	0.20	0.002	0.19
Chlorine.	0.07	2.07	0.21
All other elements.	0.93	0.098	0.93
	100.00	100.000	100.00

10. Mixtures and Compounds. — We must define the word “compound” more exactly, and distin-

guish it from “**mixture.**” The rock, *granite*, is a *mixture of minerals*. The glassy *quartz*, flaky *mica*, and pink or white *feldspar* can readily be distinguished in it. Sometimes there is also a black ingredient, *hornblende*. All of these may be picked out by mechanical means, and no chemical change is required to separate them. *Most rocks and soils are mixtures*, as granite is, of several ingredients.

The constituents of granite, just named, are all *compounds*. We may also have mixtures of elements. If we grind iron and sulphur together in a mortar, using 7 grams of iron for every 4 of sulphur, we get a mixture the color of which is a blend of the colors of the two elements. Even though the materials are mixed with great care, the microscope reveals the unchanged particles of iron and sulphur lying side by side. A magnet still attracts the iron. We can separate the iron and sulphur most conveniently by using the liquid, *carbon disulphide*. This dissolves the sulphur, but not the iron. If the mixture of carbon disulphide, sulphur, and iron is poured upon a filter, the **filtrate** (what passes through) consists of carbon disulphide and sulphur. The **residue** upon the filter paper is the iron. When the carbon disulphide is allowed to evaporate, the sulphur remains. The elements mixed in the mortar were separated by a physical operation; they had not united to form a compound.

If some of the mixture of iron and sulphur is

heated, a **chemical reaction** is started. The mass becomes very hot, and glows brightly. When the product of the reaction is examined, it is found to be neither iron nor sulphur, as judged by its properties. The magnet does not attract it. Carbon disulphide does not dissolve the sulphur. The iron and sulphur have united to form a compound, *ferrous sulphide* (cf. § 106). They might have been ground together in any proportion to form a *mixture*, but to form ferrous sulphide they unite in the proportion of 7 parts, by weight, of iron to 4 parts of sulphur. Any excess of either would simply be left over, uncombined.

We may summarize the differences between mixtures and compounds thus:

1. In a *mixture* the ingredients may be present in *any* proportion. In a **compound** the elements are united in **definite proportions** (cf. § 65).

2. When a mixture of elements is made there is generally no energy change. The formation of a compound is usually accompanied by an energy change, i. e., evolution or absorption of heat (cf. § 27).

3. The ingredients of a mixture may be separated by mechanical means. The elements of a compound can be separated only by some chemical change.

Mixtures are sometimes called *physical*, or **mechanical mixtures**.

II. The Field of Chemistry. — Both Physics and Chemistry deal with matter and its changes. But

Physics considers especially the changes in which the composition of the substance is not altered, while Chemistry is concerned with those that result in *new substances*. The study of substances and their properties is thus the particular field of Chemistry. Many substances occur in the earth, but many others must be made in the laboratory, or on a commercial scale. But the occurrence, preparation, and properties of elements and compounds are *only a part* of what we study in Chemistry. There are *rules* according to which substances react; these are the **Laws** of Chemistry (*cf.* §§ 65 and 94). *To explain a rule* or law we devise a **theory**, or *hypothesis* (*cf.* §§ 95 and 141).

12. Importance of Chemistry. — A knowledge of Chemical Science is **necessary** for the intelligent study of other natural sciences, such as geology, astronomy, biology, physiology, etc., for these sciences make *special* applications of the ideas of Chemistry. Chemistry is also **very practical**, for the facts and methods it teaches are in the most common use in the arts and in every-day life. It finds application in medicine, in sanitation, in domestic science, in the extraction of metals from their ores, in the refining of petroleum and coal tar, and in the manufacture of steel, illuminating and fuel gas, paints, dyestuffs, food products, ice, alcohol, soap, glass, paper, explosives, etc.

13. Exercises.

1. Classify the following as either physical or chemical changes: the souring of milk, the burning of wood, the evaporating of water, the tarnishing of silver, the dissolving of sugar in water, the bleaching of muslin, the melting of lead.

2. Give all the physical properties you know of the following substances: lead, wood, sugar, coal, gold, iron.

3. Give the chemical properties of the substances of 2.

4. What reason is there for considering silver an element?

5. Name some *physical* changes brought about by means of electricity, of light, and of heat. Name some chemical changes brought about by the same agents.

6. Learn the metric tables for length, volume, and weight (Appendix i).

7. How many cubic centimeters in a liter? In 1 c.dm.? State the relation between g., mg., dg., cg., kg. Between mm., cm., dm., and m.

8. In what way are the metric units of length, weight, and volume connected?

9. What is the weight of 106 c.c. of water? Give the volume, in c.c., of 30 g. water. Of 30 g. platinum of S.G. 21.5. Of 30 g. ether of S.G. 0.72.

CHAPTER II.

. OXYGEN.

14. The Air and Chemical Change. — Since air is a gas, and hence difficult to handle, men were slow in learning how it is connected with the important chemical changes that take place only when it is present. Among these changes are the *respiration* of animals and plants, the *fermenting* of fruit juices, the *decay* of wood and other organic materials (cf. § 25), the *tarnishing* of metals, and the *burning* of combustible substances. When the relation of air to these changes was once recognized, the progress of science was rapid.

15. Rusting of Metals. — Most metals undergo *tarnishing*, or **rusting**, either at ordinary or at elevated temperatures. This had been known for many centuries, but it was Jean Rey who first noticed, in 1630, that given amounts of the metals increase in weight when the metals rust, and who first stated that contact of the metal with air was the probable cause. Other investigations led to the same conclusion. However, Rey's explanation of rusting was not accepted and applied until restated

by Lavoisier, in 1774. Lavoisier sealed a weighed quantity of tin in a flask, and heated it for several days. He noticed that the tin was partly changed into the white powder which had been studied by Rey. Although a chemical change had evidently occurred inside the flask, no change in weight could be noticed. But when the flask was opened, a certain amount of air rushed in. This showed that the tin rusted by taking up something from the air in the flask.

16. Priestley and Lavoisier. — In the same year in which Lavoisier made his important experiment with tin, Priestley, in England, prepared the gas which tin and other metals take up from the air. Priestley filled a glass vessel (Fig. 2) with mercury and floated various substances to the top of the mercury. He then heated them by means of a burning glass. One of the substances was the red powder, *mercuric oxide*. It can be made by heating mercury

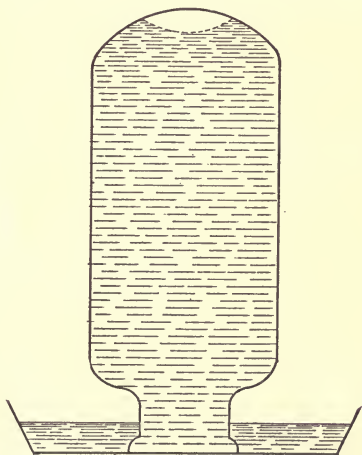


FIG. 2.

for a long time, in the air, at a temperature just below the boiling point of mercury (357° C.). By heating mercuric oxide Priestley obtained *oxygen*, a colorless gas which supported burning better than air, and which could be breathed without harm by mice. Priestley called the gas "good air." The date of the discovery of oxygen was August 1, 1774. Lavoisier, with his own recent experiments in mind, concluded that the gas Priestley had discovered was the very constituent of the air that caused the rusting of metals. So Lavoisier devised the following experiment (Fig. 3):

A retort containing some mercury was in communication with a bell-jar the mouth of which was closed by mercury. There was thus an enclosed quantity of air in the retort and bell-

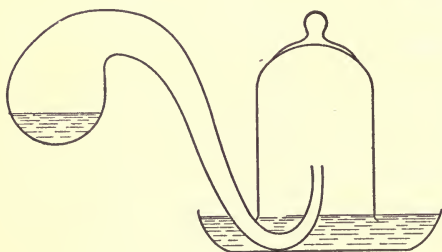


FIG 3.

jar. The mercury of the retort was heated in contact with this air for twelve days. As the heating continued, the surface of the mercury became covered with the red powder, and the air diminished to about four fifths of the

original volume. The gas remaining no longer supported life or burning. It was, in fact, **nitrogen** (cf. § 186), so called because it is a constituent of *niter*, or saltpeter.

When Lavoisier removed the red powder from the mercury,

and heated it, it was broken up into mercury and Priestley's "good air." The volume of this gas was just equal to the volume lost by the air. Lavoisier named the new gas **oxygen**, i. e., "acid-former," because he thought it was present in all acids.

Scheele (Shālā), a Swedish chemist, undoubtedly prepared oxygen in 1771-1773, but his results were not published until later. He obtained it from manganese dioxide, from niter, and from mercuric oxide.

17. Burning in the Air. — When metals unite with oxygen, the products (oxides) are solids and readily handled. But when ordinary combustibles, such as wood, wax, and illuminating gas, are burned, the products are gaseous and escape observation. Yet the chemical change is essentially the same as in the rusting of metals: it is the *union of the substances burned with the oxygen of the air*.

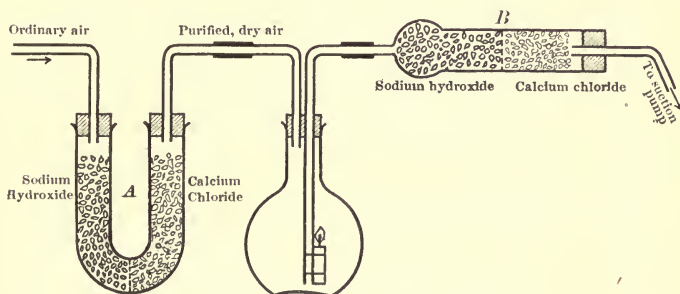


FIG. 4.

The apparatus of Fig. 4 enables us to prove that the products formed in the burning of a candle weigh more than the candle.

The flask, connecting tubes, etc., and straight drying tube (B) are weighed on the balance. The candle is then lighted, the stopper replaced in the flask, and the U-tube (A) is attached. Air is now drawn through the apparatus by a suction pump. The candle should continue to burn. The tube (B) contains sodium hydroxide and calcium chloride to catch the products (carbon dioxide and water) formed as the candle burns. The U-tube also contains sodium hydroxide and calcium chloride to remove any carbon dioxide or water from the air. Although the candle wastes away, the apparatus gains in weight because of the oxygen taken from the air.

18. Per Cent of Oxygen in Air. — The experiment of Lavoisier showed (§ 16) that air is about one fifth oxygen, by volume. More careful experiments confirm Lavoisier's conclusion. Instead of heated mercury, yellow phosphorus may be used at the ordinary temperature (Fig. 5). The air ceases to shrink in

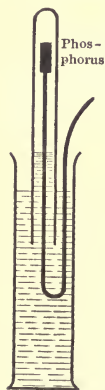


FIG. 5.

volume when practically 21% has been removed. This is the volume of the oxygen. The phosphorus and oxygen unite to form *phosphorus pentoxide*, a white solid that dissolves readily in water.

19. Preparation of Oxygen. — The oxygen used in the laboratory is usually obtained by heating *potassium chlorate* to 350°–400° C. Potassium chlorate is 39.18% oxygen, by weight, and all the oxygen is given off if sufficient heat is applied.

(See, however, § 332 for the intermediate formation of potassium *perchlorate*.) Potassium chloride is not volatile at the temperature used and remains behind.

Potassium chlorate $\longrightarrow$ potassium chloride + oxygen.

Com-
posed
of { potassium,
chlorine,
oxygen.

Com-
posed
of { potassium,
chlorine.

20. Common Laboratory Method. — Oxygen is produced much more easily, and at about 200° C., if we heat, not potassium chlorate alone, but potassium chlorate mixed with manganese dioxide, or with ferric oxide. This is the *common laboratory method* (Fig. 6). The gas is collected in bottles

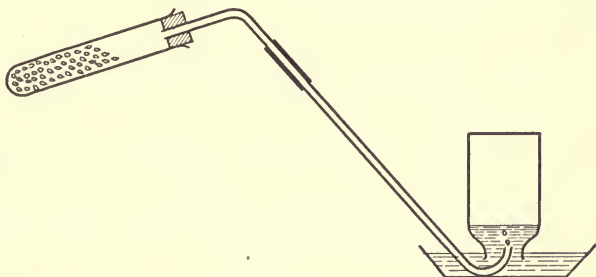


FIG. 6.

filled with water and inverted in a water pan (called, also, *pneumatic trough*).

In the decomposition of potassium chlorate, as in all chemical reactions, there is a *definite relation* be-

tween the **weights** of the substances taken and of those formed (*cf.* **Law of Definite Proportions**, § 65). Since 39.18% of potassium chlorate is oxygen, and all of it is liberated, we can always calculate that 100 grams of potassium chlorate will give 60.82 grams of potassium chloride and 39.18 grams of oxygen.

21. Catalytic Action. — The manganese dioxide (or ferric oxide) used to increase the speed of decomposition of potassium chlorate is not permanently changed in the experiment, but may all be recovered. A substance which affects a reaction merely by its presence, without itself being used up, is called a **catalytic**, or *contact*, **agent**, and the action is called **catalysis**, or *contact action*.

22. Other Methods. — Other methods of preparing oxygen are:

(1) Decomposition of water by the electric current (§§ 57 and 61).

(2) Decomposition of mercuric oxide by heat. This is the historic method of Scheele, Priestley, and Lavoisier (§ 16). Mercuric oxide is 7.41% oxygen, by weight.

(3) Decomposition of barium peroxide. Barium peroxide is a white solid that is 18.9% oxygen. It gives up *half* of its oxygen when heated, and *barium monoxide* remains.

Barium peroxide $\longrightarrow$ barium monoxide + oxygen.

A commercial method of preparing oxygen (Brin's process) is to heat *barium monoxide* to about 700° C., at increased pres-

sure, in a *current of air*. The barium monoxide and oxygen unite, giving *barium peroxide*. The air current is then cut off and the pressure lowered. As a result the barium peroxide is decomposed into barium monoxide and oxygen. The oxygen is collected and stored. When the pressure is raised once more, and the air current is passed over the barium monoxide, the reverse change — combination of barium monoxide and oxygen — again takes place.

(4) Decomposition of manganese dioxide. Manganese dioxide is 36.9% oxygen. At about 600° C. it gives off one third of it. Manganous-manganic oxide remains. Manganese dioxide is found in nature as the mineral **pyrolusite** (*cf.* § 500).

23. Physical Properties. — Pure oxygen is colorless, tasteless, and odorless. It is somewhat heavier than air, and 16 times as heavy as hydrogen (*cf.* § 51). One liter of it weighs 1.429 grams at 0° C. and 760 mm. pressure (*cf.* Appendix v). About 3 c.c. of oxygen dissolve in 100 c.c. of water under ordinary conditions (*cf.* § 83).

Gaseous oxygen may be condensed at -118° C. and 50 *atmospheres* pressure — i. e., 50×760 mm. (*cf.* § 36), to a bright blue liquid having magnetic properties. This may be solidified.

24. Chemical Properties. — The chief chemical property of oxygen is its power of uniting with other elements to form **oxides**. This property is shown in the rusting and tarnishing of the metals (*cf.* § 15), and in the energetic way in which combustibles burn

in oxygen. Thus, a pine splinter which is merely *glowing* in the air will burst into flame if put into oxygen. Burning in the air is more slow because the oxygen is diluted with inert gases (chiefly *nitrogen*, cf. §§ 186 and 190) which do not support ordinary burning at all. Iron burns in oxygen with brilliant *scintillation*, forming a black solid, *magnetic iron oxide* (cf. § 492); charcoal burns with a *glow*, as in air, but much more brightly; calcium, magnesium, phosphorus, and sulphur burn with intensely brilliant flames to give calcium oxide (quicklime), magnesium oxide, phosphorus pentoxide, and sulphur dioxide, respectively. Calcium oxide, magnesium oxide, and phosphorus pentoxide are white solids. Sulphur dioxide and carbon dioxide are colorless gases. Sulphur dioxide has the characteristic odor of burning sulphur. Many of the elements are found in nature as *oxides*. *Water* is *hydrogen oxide*. Fluorine and the argon family alone (cf. §§ 317 and 191) form no oxygen compounds.

25. Oxidation. — To the union of oxygen with other substances, *whether elements or compounds*, we give the name **oxidation**. The substance that combines with oxygen is said to be **oxidized**. A substance that gives up its oxygen to another is called an **oxidizing agent**. *Potassium nitrate* is an oxidizing agent. Gunpowder, a mixture (cf. § 232) of potassium nitrate, charcoal, and sulphur, owes its rapid

reaction (explosion) to the fact that the potassium nitrate *oxidizes* the charcoal and sulphur.

Oxidation may be *rapid*, or it may be *slow*. Thus, a piece of magnesium may burn up rapidly in oxygen, giving magnesium oxide (§ 24) and, besides, much heat and light, or it may be changed slowly (rust), when exposed to moist air, *into the same product*, without evolution of light and, apparently, without liberation of heat. Yet the energy set free in the one case is the same as in the other. There is no perceptible rise of temperature in the slow oxidation because the heat is dispersed as rapidly as it is set free. **Decay**, as of wood, is a form of slow oxidation; so is the rusting of iron. Decay takes place only in the presence of certain oxidizing bacteria (*cf.* § 230).

26. Combustion. — Burning, or *combustion*, in air is simply **rapid oxidation** (§ 17). The phenomena of heat and light accompany combustion because energy is given off much more rapidly than it can be dispersed. As a result the burning body becomes hot. The *products of combustion* are chiefly *oxides*. Because a combustion started in air continues in oxygen, oxygen is said to be a *supporter of combustion*.

Combustion in air or oxygen is not different from any other chemical union producing heat and light, such as the case of iron and sulphur (*cf.* § 10). Other gases may be supporters of combustion just as truly

as oxygen. Thus, phosphorus burns in chlorine (*cf.* § 118).

Deflagration is *very rapid combustion*, such as that of gunpowder. When charcoal and sulphur burn in the air or oxygen, the oxidation takes place *at the surface*, where the oxygen is in contact with the combustible. But in gunpowder (*cf.* § 25) the oxygen (contained in the potassium nitrate) is so close to every part of the combustibles that the oxidation takes place almost instantly *through the whole mixture*. In an enclosed space, the gases formed are under great pressure. When released, they are capable of hurling a projectile, or of tearing apart masses of rock.

27. Energy and Chemical Change. — In § 6 it was stated that coal has *chemical energy*, because heat is liberated when it is burned. The same is true for the other combustibles described in this chapter. Not only in oxidation, but in many other chemical changes, heat is given off (*cf.* § 10). Whence comes this energy?

We must assume that a substance (element or compound) consists not only of matter, but also of **energy** associated with the matter. Carbon is not only the carbon *matter*, but the *matter plus energy*. Oxygen, as we know it, is the elementary material **and** energy. When carbon and oxygen unite, the resulting compound, *carbon dioxide*, cannot hold all the energy originally associated with its two constituents, hence some energy is set free. Similar reasoning applies in other cases.

The compounds that are formed with the evolution of much energy are very **stable**, i. e., *they are decomposed with difficulty*. Thus, water and carbon dioxide are very stable compounds (*cf.* § 311).

28. Flames. — *A flame is a gas in combustion.* To burn with a flame a substance must either be gaseous itself, or it must evolve gaseous combustibles. Magnesium, sulphur, phosphorus, and wax burn with flames because they are first converted into the gaseous form; wood and soft coal, because they give off combustible gases (*cf.* illuminating gas, § 297); but charcoal and coke, which contain practically no volatile constituents, merely *glow*.

29. Kindling Temperature. — The temperature at which a combustible begins to burn is called its *kindling*, or **ignition**, *temperature*. Thus, yellow phosphorus ignites at about 40° C., in air, and sulphur at about 260° C. The heat given off in the burning of one part of a substance raises the temperature of adjacent parts to the ignition point, as in the burning of wood, paper, etc. In the match the head is ignited by friction, and the heat generated by the burning of the head ignites the wood.

The burning body must be kept at, or above, the kindling temperature, or combustion will cease. A candle burning in an enclosed portion of air goes out when the oxygen falls below 17%. With so little oxygen present, heat is not evolved rapidly enough to maintain the ignition temperature. But with phosphorus

the heat evolution is more rapid, and the product of combustion is a solid (cf. § 24) which does not *dilute* the oxygen remaining, hence burning goes on until all the oxygen is used up.

A moderate draft of air is favorable to combustion, because it brings fresh oxygen and removes the nitrogen and the products of burning. But a too rapid current will cool the burning-body below the kindling temperature. Thus, a flame may be "blown out" by a gust of air.

30. The Safety Lamp. — The lowering of the temperature below the kindling point is admirably illustrated in the **safety lamp** invented by Sir Humphry Davy to prevent explosions of "fire-damp" — a mixture of marsh gas (§ 292) and air — in mines. The lamp (Fig. 7) consists of an ordinary lantern entirely surrounded by wire gauze. When it is brought into an explosive gaseous mixture, the gases diffuse through the wire gauze, and burn *inside* the lamp, but the heat produced is conducted away by the gauze, so that the gases *outside* do not reach the ignition temperature. A series of small explosions *inside* the lamp warns the miner of his danger.

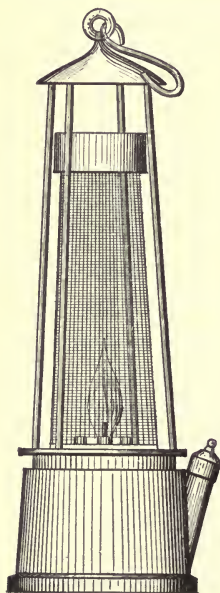


FIG. 7.

31. Spontaneous Combustion. — Even in *slow* oxidation the kindling temperature may be reached if the heat generated is not dispersed. This fact explains “spontaneous combustions,” in which oily rags, waste, etc., take fire without apparent cause. The linseed oil of paint becomes hard by absorbing oxygen from the air. Ordinarily the heat produced by the oxidation is dissipated, but when the rags are piled in heaps this is not possible, hence the temperature rises to the point of ignition. Coal packed closely in poorly ventilated bunkers often takes fire because of slow oxidation.

Spontaneous combustion may be illustrated by means of a solution of phosphorus (only a small amount must be used) in carbon disulphide. If this solution is poured upon a filter paper supported on a ring stand, the phosphorus will soon take fire “spontaneously.” The explanation of the phenomenon is that the evaporation of the carbon disulphide leaves the phosphorus in the pores of the paper, where it is oxidized. The heat generated, being prevented from escaping by the non-conducting filter paper, soon raises the temperature of some part of the paper to the ignition temperature of the phosphorus.

32. Reversed Combustion. — If both the combustible and the supporter of its combustion are gaseous, the combustion may be *reversed*. Thus, oxygen may become the burning body and illuminating gas the supporter of combustion. This reversal may be shown by a very simple experiment.

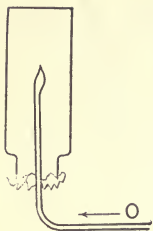


FIG. 8.

A bottle (Fig. 8) is supported, mouth downward, and filled with illuminating gas by displacing the air. The gas at the mouth of the bottle is then lighted, and while it is burning a jet of oxygen is brought up into the bottle. The oxygen takes fire at the bottle's mouth and burns in the atmosphere of illuminating gas. The oxygen jet may be replaced by a combustion spoon of potassium chlorate which has been heated so that it gives off oxygen.

33. Importance and Uses of Oxygen. — As the table in § 9 shows, oxygen makes up 47% of the earth's solid crust and nearly 86% of the ocean. Eight ninths of water is oxygen (§ 64), and about 23%, by weight, of the atmosphere.

Practically all living things require oxygen for their **respiration**. Water animals get it from the air dissolved in the water. The object of respiration is to get oxygen in contact with worn-out tissues, so that they may be converted into products which the organism can readily eliminate. Among these is the gas *carbon dioxide* (cf. § 281). The heat generated in these oxidations keeps the bodies of the higher animals warm (§ 25). In certain diseases the lungs are not able to supply the body with oxygen rapidly enough from the air, so pure oxygen is used.

While plants use oxygen, and give off carbon dioxide, just as animals do, yet they carry on the reverse action, i. e., use up carbon dioxide, and give

off oxygen, in building up their tissues. The carbon dioxide and water used by plants for this purpose together contain too much oxygen, hence the excess is given off to the air. Animals and plants are thus *interdependent*, the one giving off what the other uses. As a result the quantity of oxygen in the air is kept practically constant.

34. Exercises.

1. How many grams of mercury and of oxygen will be formed by the decomposition of 43.2 grams of mercuric oxide?

2. How many grams of manganese dioxide are needed to give, when decomposed by heat, 12 grams of oxygen? How much manganous-manganic oxide will be formed?

3. Calculate the weight of potassium chlorate that will produce, when heated, 74.5 grams of potassium chloride. What weight of oxygen is formed at the same time?

4. How many cubic centimeters of oxygen can be made from 1.2 grams of potassium chlorate if 1 c.c of the gas weighs .0014 gram?

5. How many grams of potassium chlorate must be decomposed to give 36 liters of oxygen when 1 liter of oxygen weighs 1.25 grams?

6. What weight of oxygen can be obtained from 50 grams of water? What volume will it have at 0° C. and 760 mm.?

7. Name the materials used in starting a coal fire. In lighting a gas stove. What are the causes of the difference?

8. Name the oxides used as sources of oxygen in the order of their *stability* toward heat, beginning with the least stable one. Where would you place potassium chlorate?

9. Devise an experiment to prove that part of the air disappears in the rusting of iron.

CHAPTER III.

MEASUREMENT OF GASES.

35. The Volumes of Gases. — Because it is difficult to weigh gases accurately their quantity is usually given, *not* in weight units, but in units of volume, such as the *cubic centimeter*, or the *liter* (*cf.* Appendix i). Hence it is important that the volumes of gases be determined with great accuracy. Now, experiments with gases must often stand for hours, or over night. Meanwhile the temperature and pressure, and, consequently, the volume, undergo change. Cooling will contract the volume; heating expands it. Increase of pressure will make the volume smaller; a lowering of pressure will increase the volume. So the chemist must be able to calculate what the volume of a gas, measured at *any* temperature and pressure, will be at *any other* temperature and pressure.

36. Measurement of Pressure. — Pressure of gases is measured in **atmospheres**, or in *millimeters of mercury*. The instrument used for measuring atmospheric pressure is the *barometer* (Fig. 9). The simple barometer consists of a glass tube about a meter long, closed at the upper end, and partly

filled with mercury. It stands in a bath of mercury. When the barometer is made, the glass tube is entirely filled with mercury. The open end is then covered with the finger, the tube is inverted in the mercury bath, and the finger is removed *under* the mercury. The mercury in the tube flows out until the level inside the tube is about 760 mm. (30 inches) above that in the bath. It does not fall out entirely because the air pressure sustains it. The height of the mercury column changes with the atmospheric pressure. Its average at sea-level is 760 mm. This is **standard pressure**, or a pressure of *one atmosphere*.

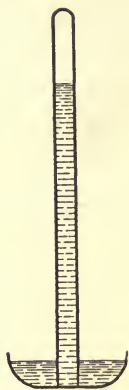


FIG. 9.

A column of mercury 760 mm. high and 1 sq. cm. in cross sectional area weighs 1,033.6 grams; hence this is the pressure of the atmosphere upon 1 sq. cm. at sea level. If the liquid used is water, which is $\frac{1}{13.6}$ as heavy as mercury, the height of the barometer will be *13.6 times as great* as with mercury, *i. e.*, 10.4 meters, or 34 feet.

37. Temperature. — Temperature is usually measured by the mercury thermometer graduated on the Centigrade scale. The **zero** mark is determined by immersing the bulb in *melting ice*. The 100° mark is the temperature of *water boiling under standard pressure*. The space on the thermometer stem lying between these two marks is divided into 100°

and the degrees are marked off above and below the two fixed points. As mercury boils at 357° C. and freezes at -40° C. the interval between represents the range of an ordinary chemical thermometer.

COMPARISON OF ORDINARY WITH ABSOLUTE SCALE.

	FAHRENHEIT.	CENTIGRADE.	ABSOLUTE SCALE.
Mercury boils.	672.6°	357°	630°
Water boils.	212°	100°	373°
Room temperature.	68°	20°	293°
Water freezes.	32°	0°	273°
Mercury freezes.	-39.1°	-39.5°	233.5°
Oxygen boils.	-296.5°	-182.5°	90.5°
Nitrogen boils.	-315°	-194°	79°
Hydrogen boils.	-422.5°	-252.5°	20.5°
Absolute Zero.	-459.6°	-273°	0°

38. Volume and Temperature; Charles' Law. — If the volume of **any** gas is read at 0° C., and the gas is then heated, the volume will be increased $\frac{1}{273}$ (i. e., 0.00366) of the volume at 0° C. for every degree the temperature is raised above 0° C. It will also shrink $\frac{1}{273}$ of the volume at 0° C. for every degree it is cooled below 0° C. *This is Charles' Law.*

A volume of 100 c.c., measured at 0° C., will thus become $100 \times 1\frac{1}{273}$ at 1° C., and $100 \times 1\frac{20}{273}$ at 20° C. At -20° C. its volume would be $100 \times \frac{253}{273}$, that is, $100(1 - \frac{20}{273})$. At 273° C. its volume would be *twice* what it was at 0° C., while at -273° C. its volume would be **0**. This last temperature (-273° C.) is

called the **Absolute Zero**. Before it is reached all gases become liquid or solid. Instead of calling the melting point of ice 0° , we may place the zero point 273° below this, that is, at *Absolute Zero*. The temperature scale thus produced is called the **Scale of Absolute Temperature**, and its readings are called *absolute readings*. Centigrade readings may be changed to absolute readings by the algebraic addition of 273; 0° C. thus becomes 273 Abs., -20° C. becomes 253° Abs., and 20° C. becomes 293° Abs.

We have just learned that 100 c.c. of a gas at 0° C. become $100 \text{ c.c.} \times 1\frac{270}{273}$ at 20° C. But multiplying by $1\frac{270}{273}$ is the same as multiplying by $\frac{293}{273}$, and this is the ratio of the *absolute temperatures* corresponding to 20° C. and 0° C. The Law of Charles may now be stated in terms of the *Absolute Temperature*: —

Under constant pressure, the volume of a gas is proportional to its absolute temperature.

39. Application of Charles' Law. — Charles' Law enables us to calculate what volume a gas, measured at *any given* temperature, would occupy at *any other* temperature. Some problems illustrate the method: —

Problem 1. A gas measuring 80 c.c. at 0° C. is heated to 20° C. What volume will it have?

Solution. Let x = the volume at 20° C. The absolute temperature of 0° C. is **273**; that of 20° C., **293**. The gas is heated, hence its *volume* will be **increased**. The volume at 0° C. (80 c.c.) must be multiplied by $\frac{293}{273}$ to give the volume at 20° C.

$$x = 80 \times \frac{273}{273}.$$

$$x = 85.8 \text{ c.c.}$$

Problem 2. If 60 c.c. of oxygen, measured at 30°C. , are cooled to -10°C. , what will the volume become?

Solution. Let x = the volume at -10°C.

$$30^{\circ} \text{C.} = 303^{\circ} \text{ Absolute.}$$

$$-10^{\circ} \text{C.} = 263^{\circ} \text{ Absolute.}$$

The gas is to be *cooled*, hence the volume will be *diminished*; the new volume will be $\frac{263}{303}$ of the original volume.

$$x = 60 \times \frac{263}{303}.$$

$$x = 52.08 \text{ c.c.}$$

40. Volume and Pressure; Boyle's Law. — If the temperature of a gas is kept constant, the *volume varies inversely as the pressure*. This is **Boyle's Law**. It expresses the fact that if a gas occupies a given volume at 760 mm. pressure it will have twice this volume at 380 mm., and half the volume at 1520 mm.

The product of the number representing the volume of a gas and the number representing the pressure under which the volume is measured is, therefore, a constant; or,

$$v \times p = \text{constant.}$$

Since increasing the pressure will *diminish* the volume of a gas, it will plainly *increase* the mass of gas in a given volume, i. e., *the density*. Hence Boyle's, or, as it is sometimes called, **Mariotte's Law**, may be stated thus: *The density of a gas at constant temperature is proportional to the pressure.*

41. Application of Boyle's Law. — By using Boyle's Law we can calculate what a volume of gas, measured under a *given* pressure, will become under *any other* pressure.

Problem 1. A gas measures 120 c.c. when the pressure is 725 mm. What volume will it have at 760 mm.?

Solution. Since volume varies inversely as pressure, the gas in question will be *diminished* in volume, for the new pressure is the greater. Let x = the volume at 760 mm. The volume at 725 mm. (120 c.c.) must be multiplied by $\frac{725}{760}$ to give the volume at 760 mm.

$$x = 120 \times \frac{725}{760}.$$

$$x = 114.5 \text{ c.c.}$$

Problem 2. What will be the volume at 650 mm., of a quantity of nitrogen that measures 50 c.c. at 820 mm.?

Solution. Since the *pressure is diminished*, the new *volume* (x) will be *larger* than 50 c.c.

$$x = 50 \times \frac{820}{650}.$$

$$x = 63.08 \text{ c.c.}$$

42. Correction for Both Temperature and Pressure. — If we wish to determine the effect of changes in **both** temperature and pressure we can make the calculation for each change separately, or we can combine the two in one expression.

Problem. I have 100 c.c. of air at 20° C. and 720 mm. What will its volume be at 0° C. and 800 mm.?

Solution 1. (a) Let us make the correction for *temperature only*, and let x = the volume at 0° C. and 720 mm. Then, since the air is to be at a lower temperature, x will be less than 100 c.c.

$$x = 100 \times \frac{273}{293}.$$

$$x = 93.17 \text{ c.c.}$$

(b) Now, let us make the correction for pressure, and let y = the volume at 0° C. and 800 mm. Since the pressure is to be *increased* from 720 to 800 mm., the volume will be *diminished*, and y will be less than x .

$$y = 93.17 \times \frac{720}{800}.$$

$$y = 83.85 \text{ c.c.}$$

Solution 2. It is better to combine the two parts of Solution 1 into one operation. Let x be the volume at 0° C. and 800 mm.

Then

$$x = 100 \times \frac{273}{293} \times \frac{720}{800}.$$

$$x = 83.85 \text{ c.c.}$$

43. Correction of the Barometer Reading.—Two corrections of the barometer reading are necessary for accurate work with gases:

(1) *Correction for Temperature.*—The standard height of the barometer is 760 mm. at 0° C. Owing to the expansion of mercury when warmed, the column in the barometer is about 3 mm. longer at 20° C. than at 0° C. ; hence this amount should be subtracted from the barometer reading at 20° C. if the volume of a gas is to be “reduced” to 0° C. The table of temperature corrections is given in Appendix xii.

(2) *Correction for Water Vapor.*—When a gas is collected over water it is saturated with water vapor (steam). The pressure exerted by the moist

gas is thus made up of two **partial pressures**: that of the dry gas and that of the steam. If we wish to get the true (partial) pressure of the dry gas, we must *subtract from the barometer reading the pressure of the water vapor*. The pressure of the vapor increases with the temperature; at 100° C., the boiling point of water, it is 760 mm. (*cf.* § 71). The table of vapor pressures, reduced to millimeters of mercury, is given in Appendix v. When a gas is collected over mercury the partial pressure of the mercury vapor is considered 0.

In collecting gases over liquids the levels of liquid inside and outside are assumed to be the same; otherwise the pressure of the gas is not equal to that shown by the barometer.

A **problem** will show how the correction for the pressure of water vapor is applied.

Problem. The volume of a gas collected over water is 50 c.c. at 26° C. and 742 mm. What is the volume (x) of the dry gas at 0° C., and under 760 mm.?

Solution.

Volume of gas.....	50 c.c.
Temperature.....	26° C.
Pressure (uncorrected).....	742 mm.
Pressure of water vapor at 26° C.....	22 mm.
Partial pressure of dry gas.....	720 mm.
Absolute temperature of 26° C.....	299°
Absolute temperature of 0° C.....	273°

Therefore,
$$x = 50 \times \frac{273}{299} \times \frac{720}{760}.$$

44. Problems Involving Standard Temperature and Pressure. — The weight of a liter of a gas is always given in the tables (Appendix v) for the dry gas at 0° C. and 760 mm., i. e., for *standard temperature and pressure*. If the volume is measured at any other temperature and pressure (and it usually is) the volume must be **reduced to standard conditions** before the weight can be calculated.

Problem 1. What is the weight of 100 c.c. of oxygen measured over water at 20° C. and 720 mm.?

Solution. First, we find the volume (x) of the dry gas at 0° C. and 760 mm. The partial pressure of the water vapor is 17 mm., hence that of the dry gas is 703 mm. The equation for reducing the volume to standard conditions is, —

$$x = 100 \times \frac{273}{293} \times \frac{703}{760}.$$

Whence

$$x = 86.18 \text{ c.c.}$$

The table shows (Appendix v) that one liter (1000 c.c.) of oxygen under standard conditions weighs 1.429 grams. The weight of 86.18 c.c. is, evidently $\frac{86.18}{1000} \times 1.429$, or 0.1232 g.

Problem 2. What is the volume, at 25° C. and 718 mm., of 5 grams of oxygen?

Solution. First get the volume (x) of the oxygen at 0° C. and 760 mm.

$$x = \frac{5}{1.429}, \text{ or } 3.49 \text{ liters.}$$

Then calculate what the volume (y) will be at 25° C. and 718 mm. from the equation, —

$$y = 3.49 \times \frac{298}{273} \times \frac{760}{718}.$$

If the gas is collected over water, the pressure will be, not 718 mm., but 718 mm. — 23.6 mm., or 694.4 mm., and the volume will be proportionally larger.

45. Exercises.

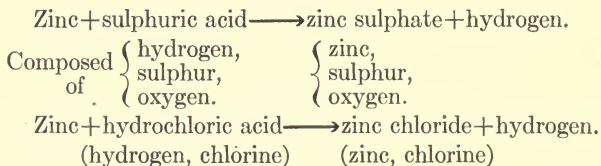
1. What will be the volume at 0°C. of a gas which at 20°C. has a volume of 90 c.c.? What volume will it have at -30°C. ? At 100°C. ? At 273°C. ? At -250°C. ?
2. 90 c.c. of air at 20°C. became 150 c.c. when heated. What was the new temperature?
3. Under a barometer pressure of 740 mm. the volume of a gas is 70 c.c. What will the volume be under 760 mm.? 650 mm.? 10 mm.? Half an atmosphere?
4. A gas measures 100 c.c. under a pressure of 400 mm. By changing the pressure the volume becomes 85 c.c. What was the second pressure?
5. A gas measures 20 liters at 10°C. and 760 mm. What volume will it have at 30° and 720 mm.?
6. A tube containing potassium chlorate was heated, and the oxygen formed was collected over water. The volume was 450 c.c. at 40°C. and 720 mm. pressure.
 - (a) What would the volume have been over mercury?
 - (b) What would the volume of the **dry** gas have been at 0°C. and 760 mm.?
 - (c) What does the oxygen weigh?
 - (d) If the heated tube lost 0.49 g., calculate the weight of a liter of dry oxygen at 0°C. and 760 mm.
7. How many liters of oxygen can be made (collected over water) by heating 122.5 grams of potassium chlorate, if the temperature is 32°C. and the barometer height 730 mm.?

CHAPTER IV.

HYDROGEN.

46. Occurrence. — Hydrogen is a colorless gas only one-sixteenth as heavy as oxygen. Very little is found *free* in the earth, but there is a great deal of it in the atmosphere of the sun. In the *combined* form it is a constituent of all living things and of most organic substances (*cf.* § 520), such as sugar, starch, petroleum, coal, and wood. The most common hydrogen compound is **water**. One-ninth of it, by weight, is hydrogen. Hydrogen is also contained in all acids and bases. The name means a “producer of water.”

47. Laboratory Method of Preparation. — The reaction between metals and dilute acids is the most convenient method of preparing hydrogen. The metals generally used are zinc and iron, and the acids, dilute hydrochloric and sulphuric acids.



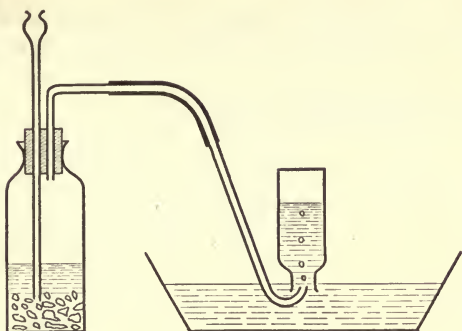


FIG. 10.

Apparatus. Hydrogen is usually generated in a bottle or flask (Fig. 10), provided with a "thistle," or "safety" tube and a delivery tube reaching to a water pan (*cf.* § 20). The metal (zinc or iron) is placed in the bottle, and acid is added through the thistle tube. The hydrogen escapes through the delivery tube, and is collected over water. Or, since hydrogen is much lighter than air, it may be collected by displacing air (Fig. 11).

Caution! *Apparatus in which hydrogen is being made must not be brought near a flame!* If the action between metal and acid is not brisk, it may be hastened by adding a few drops of copper sulphate solution. The copper sulphate reacts with a portion of the zinc, precipitating copper upon the zinc; when copper is present as a contact agent (*cf.* § 21), zinc acts readily

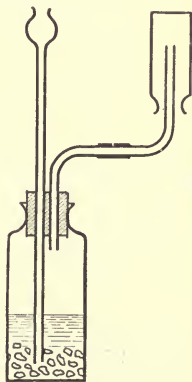


FIG. 11.

upon the acid. The action of zinc and acid results in a very considerable evolution of heat (*cf.* § 27).

48. Self-Regulating Generator.

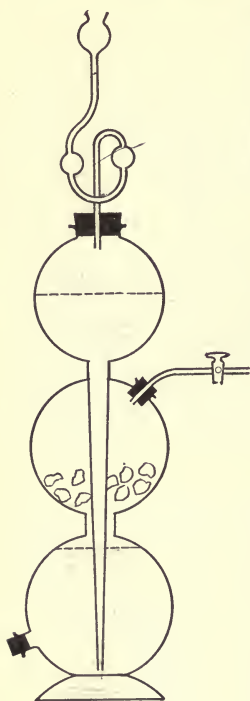


FIG. 12.

Instead of the ordinary generating flask, a Kipp's or other self-regulating apparatus may be used to supply hydrogen. Kipp's apparatus (Fig. 12) consists of three globes. The upper globe is in communication with the lower globe, and the middle globe with the lower globe, but the upper globe and the middle globe are not connected. The upper and lower globes contain dilute acid, but the middle globe contains zinc. This is the condition of the apparatus when at rest, with the stopcock closed. When the stopcock is opened, the liquid of the upper globe falls into the lower globe, and the liquid in the lower globe rises into the middle globe, thus displacing the gas of the middle globe, and forcing it out through the stopcock. The acid which enters the middle globe reacts with the zinc, forming more hydrogen, which either escapes through the stopcock, or, if the latter is closed, forces the acid back into the lower globe and thence into the upper globe. The gas in the middle globe is thus ready for instant use.

49. Purification of Hydrogen. — If the metal or the acid used in preparing hydrogen is of “com-

mercial" grade the hydrogen will be *impure*, and will have a disagreeable odor. We may remove most of the impurities by passing the gas through a solution containing *sodium hydroxide* and *potassium permanganate* (A, Fig. 13). To remove water vapor we use a **drying agent**, e. g., granular **calcium chloride** (B, Fig. 13 and § 90).

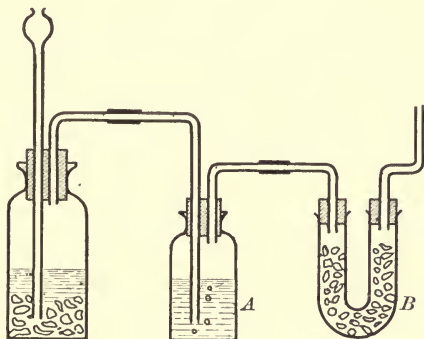


FIG. 13.

50. Precautions in Igniting Hydrogen.

Before we light a jet of hydrogen (the same precaution applies to other inflammable gases), we collect a test tube full by air displacement (Fig. 11), and then carry the test tube — in this case, mouth down — to a flame at least *four feet* (over a meter) away. The gas in the test tube burns rapidly ("explodes") if there is still much air mixed with the hydrogen, but it burns slowly if the air has been displaced. We then carry the test tube (mouth down) back to the jet of hydrogen until the gas is lighted by the test tube of burning hydrogen.

51. Physical Properties. — Hydrogen is colorless, odorless, and tasteless. It is the lightest substance known; air is 14.4 times as heavy (*cf.* Appendix v). One liter weighs only .09 gram, under standard conditions. When hydrogen is used as a standard of density for gases (*cf.* § 6), its relative density is taken as 1. Hydrogen is less soluble in water than oxygen (*cf.* § 23); at 14° C., 100 c.c. of water dissolve only 1.9 c.c. of the gas.

At the ordinary temperature hydrogen cannot be liquefied by any pressure, however great (*cf.* § 197); but at a low temperature and under great pressure the gas has been condensed to the liquid and solid state. **Liquid hydrogen** is colorless and $\frac{1}{14}$ as heavy as water. It boils at -252.5° C. **Solid hydrogen** melts at -260° C. under 58 mm. pressure.

Hydrogen is a better conductor of heat and electricity than any other gas.

52. Diffusion, or Transpiration, of Hydrogen. — When two gases, such as air and hydrogen, are brought together, they form a uniform mixture. Even if they are temporarily separated, as by a porous partition, they will pass through, and mix completely. But the lighter the gas, the more rapid its diffusion (*transpiration*) through small apertures. The rule is that *the rates of transpiration are inversely proportional to the square roots of the*

densities of the gases. Hydrogen diffuses **four times** as rapidly as oxygen. With this explanation we can understand the following:

A porous cup (Fig. 14) is attached securely to a glass tube ending under water. If, now, a jar of hydrogen is placed over, and enclosing, the porous cup, bubbles



FIG. 14.

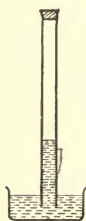


FIG. 15.

of gas will escape from the lower end of the tube. The increase of volume is due to the rapid movement of hydrogen **into** the cup. When the jar is removed the *reverse* diffusion takes place. A simpler apparatus is shown in Fig. 15. A wide glass tube has one end covered with a cap of plaster of Paris. If the tube is filled with hydrogen, by air displacement, and the open end is placed under water, water will rise in the tube.

53. Occlusion of Hydrogen. — Hydrogen is absorbed (“**occluded**,” or “hidden away”) in large quantities by certain metals, e. g., iron, platinum, and palladium. Under the best conditions one volume of palladium occludes 873 volumes of hydrogen. When gases are compressed, heat is liberated; hence in the enormous compression that takes place in occlusion the hydrogen is set on fire. A piece of platinum sponge held in a jet of dry hydrogen ignites the gas. This fact is put to use in constructing self-lighting gas burners. Occluded hydrogen can be expelled by heat.

54. Chemical Properties. — Hydrogen burns in air or oxygen to produce **water**. In chlorine it

burns to form *hydrogen chloride* (cf. § 118). It can be made to unite with nitrogen to give *ammonia* (cf. § 213), and with sulphur to give *hydrogen sulphide* (cf. § 253). When an electric arc is produced between poles of carbon in an atmosphere of hydrogen, the two elements unite to form *acetylene* (cf. § 295).

Hydrogen does not “support combustion” (cf. § 26); that is to say, burning wood, paper, illuminating gas, etc. — the ordinary combustibles — do not continue to burn when placed in hydrogen, because *they cannot unite with hydrogen*. Oxygen, however, burns in hydrogen (cf. § 32). Hydrogen is really **inert** at ordinary temperatures, hence an “atmosphere” of hydrogen is often used in experiments requiring the absence of the active oxygen of the air.

55. Union of Hydrogen and Oxygen. — At the ordinary temperature a mixture of hydrogen and oxygen may be kept for years without any evidence of action. The reaction is more and more rapid as the temperature is raised, until it becomes an “explosion” above 615°C . Finely divided platinum, acting *catalytically* (cf. § 21), causes explosive union at the ordinary temperature.

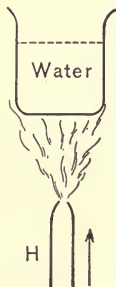


FIG. 16.

The steam formed when hydrogen burns

in air may be condensed by holding over the flame a cold object (Fig. 16), or by allowing the products of combustion to pass through a condenser (Fig. 17). A vessel of *cold* water placed over a gas flame condenses some of the steam formed in the burning of the gas.

The hydrogen flame is *colorless*, but **very hot**. One gram of hydrogen burning in oxygen (how much oxygen is needed?) liberates 34,200 **calories** of heat, i. e., enough to heat 34,200 grams of water from 0° C. to 1° C., or to heat about 340 grams from the freezing point to the boiling point.

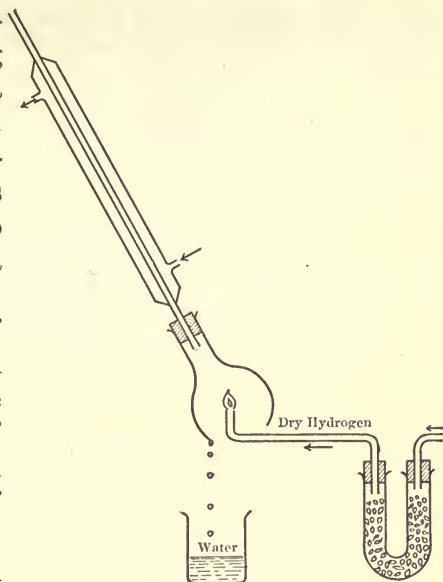


FIG. 17.

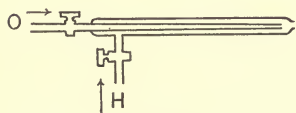


FIG. 18.

An apparatus for making use of this great heat evolution is the **oxyhydrogen** blowpipe (Fig. 18). This consists of a small inner tube communicating with a tank of

oxygen, and a larger outer tube in connection with a tank of hydrogen. Both gases are greatly compressed. The hydrogen is first turned on and lighted; then the oxygen is allowed to escape *very slowly*. Thus a flame is produced which is so hot that it will melt platinum. (Platinum melts at about 1777° C.) A piece of quicklime held in the oxyhydrogen flame becomes white hot and gives off much light; this is the so-called *calcium*, or *lime*, light. In the production of the lime light for stereopticons, illuminating gas is generally used instead of hydrogen. The ordinary **blast-lamp** of laboratories is similar to the oxyhydrogen blowpipe, but the gases used are illuminating gas and ordinary air; as a result, the temperature produced is by no means as high as that of the oxyhydrogen flame.

56. Reduction. — Hydrogen has the power of combining not only with *free* oxygen, but also, in many cases, with oxygen that is in combination with other elements. Thus, if hydrogen is passed over heated copper oxide and iron oxide, it unites with the oxygen of these substances, forming water, and setting free copper and iron respectively.

Copper oxide + hydrogen $\longrightarrow$ copper + water.

Iron oxide + hydrogen $\longrightarrow$ iron + water.

The removing of oxygen from a compound is called **reduction**, and the substance that unites with the oxygen is the **reducing agent**. Of course the reducing agent is *oxidized* (*cf.* § 25) — there is no reduction without a corresponding *oxidation*. Most oxides, and the nitrates, chlorates, etc. (*cf.* §§ 24, 229, and 331), are **oxidizing agents**; carbon

and hydrogen are common reducing agents (*cf.* § 275).

57. Other Methods of Preparing Hydrogen.—As hydrogen is present in water and in bases it may be prepared from these substances as well as from acids. The following are some of the ways:

(1) By the action of the electric current upon water (*cf.* § 61). This is called the “**electrolysis of water.**” It takes place only when the water contains small amounts of acids, bases, or salts (*cf.* § 174). The products of the electrolysis of water are hydrogen and oxygen (*cf.* § 22). Sulphuric acid is the catalyzer commonly used.

(2) By the reaction between **metals** and **water**. Some metals, such as *sodium*, *potassium*, and **calcium**, react rapidly even with **cold** water, forming hydrogen and the **hydroxides** of the metals.

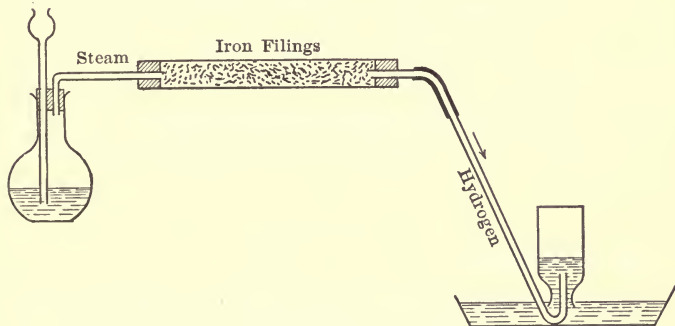
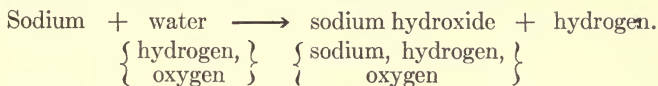


FIG. 19.

Other metals, such as magnesium, zinc, and iron, react with water rapidly only when it is **hot**, or in the form of *steam* (Fig.

19). When steam is passed over heated metals the products are **oxides** of the metals, and hydrogen.

Magnesium + water $\longrightarrow$ magnesium oxide + hydrogen.

Iron + water $\longrightarrow$ iron oxide + hydrogen.

Compare this last reaction with its reverse, § 56.

(3) By the action of metals upon **hydroxides**. Thus, aluminum filings and a solution of sodium hydroxide give hydrogen when warmed; so does a mixture of zinc dust and powdered sodium hydroxide (*cf.* § 447).

Aluminum + $\left\{ \begin{array}{l} \text{sodium} \\ \text{hydroxide} \end{array} \right\} \longrightarrow \text{sodium aluminate} + \text{hydrogen}.$
 $\left\{ \begin{array}{l} \text{sodium, alumi-} \\ \text{num, oxygen} \end{array} \right\}$

58. Uses of Hydrogen. — The uses of hydrogen depend chiefly upon its *lightness*, and upon the *high temperature* of its flame. Because of its lightness it may be used to inflate balloons. Its flame is used in the oxyhydrogen blowpipe to melt platinum and other high-melting metals, and to cause the incandescence of lime in the stereopticon light. Illuminating and fuel gases consist largely of hydrogen, either free, or combined with carbon (*cf.* §§ 296 and 299).

59. Exercises.

1. In what properties are hydrogen and oxygen alike? Unlike? If you had 3 bottles filled with oxygen, hydrogen, and illuminating gas, respectively, how could you distinguish them?

2. What properties of hydrogen make it useful for inflating balloons? What ones make it disadvantageous?

3. Under what conditions does hydrogen "explode"? What test should be carried out, and how, before a jet of it is lighted?

4. Why has not the small amount of hydrogen in the air united with oxygen?

5. What volume, in liters, have 1.008 g. hydrogen? 8 g. oxygen? If **two** volumes of hydrogen combine with **one** of oxygen, in what proportions, by weight, do they unite?

6. Calculate the relative rates of transpiration (*cf.* § 52) of two gases whose specific gravities are 36 and 16 respectively. Calculate the specific gravity of a gas which takes 4.7 times as long as hydrogen to diffuse through a porous wall.

7. A gas tank holding 100 liters is filled with hydrogen. If the temperature is 38°C. , and the pressure 690 mm., how much does the hydrogen weigh? How much water would be formed if all the hydrogen were burned?

CHAPTER V.

WATER.

60. Nature of Water.— Water is so stable that it was believed to be an element until 1781. In that year Cavendish, who had discovered hydrogen in 1766, *synthesized*, i. e., “put together,” water from hydrogen and oxygen; this proved it a compound.

61. Electrolysis of Water.— Synthesis has for its opposite, **analysis**, which means a “breaking up,” or “tearing apart,” as of a compound into its elements, or of a mixture into its ingredients. The “electrolysis of water” (*cf.* § 57, 1) is a method of *decomposition*, or analysis. It is carried out as follows:—

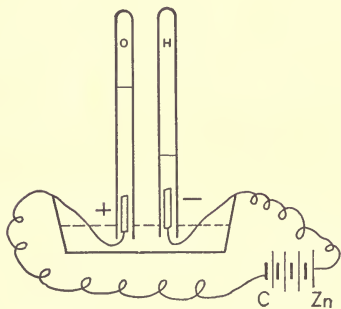


FIG. 20.

An electric current from a battery, or other source (Fig. 20), is passed between platinum electrodes through a 5% solution of sulphuric acid. The electromotive force of

the current must be over 1.47 volts. Bubbles of gas gather upon, and then rise from, the electrodes, and may be collected in tubes filled with the dilute acid and inverted over the electrodes. The electrode *by which the current enters* the solution is the **positive (+) electrode**, or **anode**; that by which the current *leaves* the solution, the **negative (-) electrode**, or **kathode**. The gas that collects at the *kathode* is considered **electro-positive**, since it is attracted by the negative charge on the kathode. The gas at the *anode* is **electro-negative**. In a given time, about **twice** as much gas collects at the kathode as at the anode. The electro-positive gas is *hydrogen*; the electro-negative, *oxygen*. The electrolysis of *sodium hydroxide* (a base), or of *sodium sulphate* (a salt), will give the same gases, in the same proportions (*cf.* § 183). While catalytic agents are necessary, it is the water itself that is decomposed.

62. Synthesis of Water, by Volume. — More decisive than electrolysis, as proof of the composition of water, is the fact that the gases hydrogen and

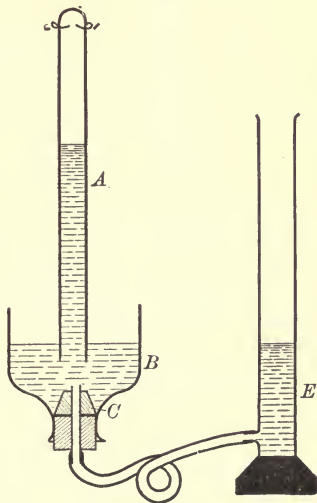


FIG. 21.

oxygen actually unite in the proportion of two volumes of hydrogen to one of oxygen to form water.

The experimental proof is as follows (Fig. 21): —

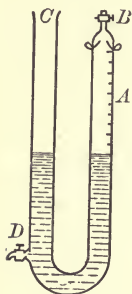


FIG. 22.

A is a "eudiometer," a strong, glass tube with two platinum wires sealed into it, near the closed end. It is filled with mercury and inverted in the bath of mercury (**B**). Some *hydrogen* is introduced into **A** under mercury. **A** is then forced securely over the rubber stopper **C**, and the hydrogen is brought to atmospheric pressure by making the mercury level in **E** the same as in **A** (cf. § 43). **A** is now slipped off from

C, and *oxygen* — a little more than the hydrogen — is introduced, and its volume is read as was that of the hydrogen. The lower end of **A** is left securely pressed over **C**, the leveler **E** is lowered so that the gases almost fill the eudiometer, and the mixture in **A** is ignited by an electric spark, obtained from a spark coil, which is passed between the platinum wires. A flash of light marks the reaction. When **A** is cool, the mercury levels are made the same, and the excess of oxygen is measured. **The volume of oxygen used up will be half that of the hydrogen taken.**

Another form of eudiometer is shown in Fig. 22. The gases are introduced into **A** through the opening controlled by **B**, and are brought to atmospheric pressure by adding mercury through **C** or by drawing it off at **D**.

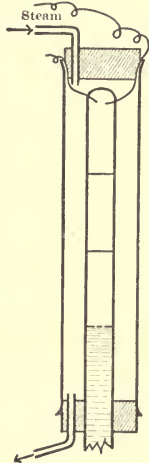


FIG. 23.

63. Relation between the Volumes of Hydrogen, Oxygen, and Steam. — The volumetric synthesis of water, as given in § 62, does not tell us the volume of the steam formed from two volumes of hydrogen and one of oxygen. This additional fact may be learned by the use of the apparatus of Fig. 21. The eudiometer must, however, be surrounded by a jacket (Fig. 23) that can be filled with steam or the vapor of some liquid boiling above 100° C.

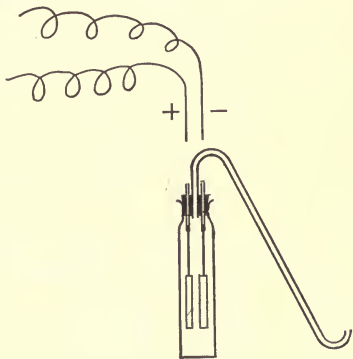


FIG. 24.

The hydrogen and oxygen are in exactly the right proportions as obtained by electrolysis. The electrolysis apparatus is shown in Fig. 24. By causing the gases to combine at, or above, 100° C. the resulting steam does not condense. **Its volume is found to be that of the hydrogen used.** This experiment was performed first by Humboldt and Gay-Lussac in 1805, and has been repeated many times. It proves conclusively that *two volumes of hydrogen unite with one volume of oxygen to produce two volumes of steam.* The facts are represented graphically by the expression: —



2 volumes hydrogen. 1 volume oxygen. 2 volumes steam.

64. Synthesis of Water, by Weight. — The exact relation, by weight, between the hydrogen and oxygen of water is of such importance that many methods have been devised to determine it.

In *one* method a known weight of hydrogen is passed over cupric oxide (*cf.* § 56). The hydrogen is oxidized to water, which is collected and weighed. The gain in weight is, evidently, due to oxygen.

In a *second* method a known weight of cupric oxide is reduced in a stream of hydrogen. *The water produced contains the oxygen lost by the cupric oxide.* The apparatus is shown in Fig. 25.

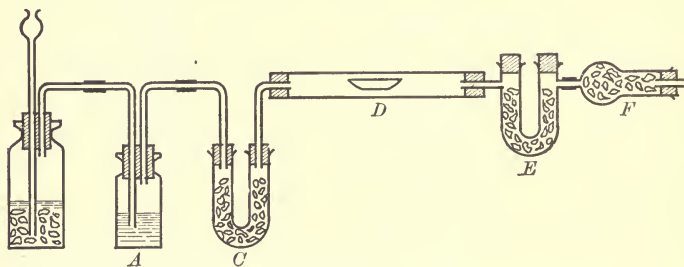


FIG. 25.

Hydrogen, purified and dried by alkaline permanganate solution (A) and calcium chloride (C) respectively, is passed over heated copper oxide contained in a porcelain boat (D), and the water produced is collected in a U-tube of calcium chloride (E). A guard tube of calcium chloride (F) excludes the water of the air.

Berzelius and Dulong carried out this experiment in 1819, with the following results: —

Weight of water taken up by calcium chloride =	30.519 g.
Loss in weight of cupric oxide (oxygen) =	27.129 g.
Weight of hydrogen united with 27.129 g. oxygen =	3.390 g.

$$\frac{3.39}{27.129} = \frac{1}{8.002},$$

the ratio of hydrogen to oxygen in water.

In a *third* method, devised by Morley, an American, the hydrogen, oxygen, and water are *all weighed*. According to Morley 1 part of hydrogen combines with 7.94 parts of oxygen, or 1.008 of hydrogen with 8 of oxygen.

65. Law of Definite Proportions by Weight. — Not only water, but *all* compounds, illustrate this definiteness of composition: or **Law of Definite Proportions**. Thus potassium chlorate is always found to have the composition: 39.18% oxygen, 31.91% potassium, and 28.91% chlorine, and mercuric oxide is always 92.59% mercury and 7.41% oxygen. The law is stated thus: —

A given chemical compound is always composed of the same elements united in the same proportions.

66. Occurrence of Water. — As was stated in § 9, the earth's great body of water, the ocean, makes up about 7% of the earth's mass. Below a certain depth, which varies greatly in different places, all soil and rock is saturated with water. The atmosphere contains a great deal (as steam).

A cubic meter of air saturated with water vapor at 20° C. contains 17 grams of it.

Water makes up a large part of all plants and animals. The human body is 70% water. Milk is 87% water, potatoes over 78%, watermelon 92%, white bread about 35%, and beef about 62%.

67. Natural Water. — Natural water, whether as snow and ice, or as liquid water, is never pure. Rain water is the purest of natural waters, but in its fall takes up dust, carbon dioxide, ammonia, etc. Water that flows over, or penetrates, the earth's surface finds many substances to dissolve. The most common *soluble solids* in natural water are salt, *magnesium chloride*, and *gypsum*. The gases most commonly present are *air*, *carbon dioxide*, *ammonia*, and *hydrogen sulphide*. Water containing carbon dioxide dissolves *limestone* (cf. § 284), hence this is usually present in natural water. Water charged with hydrogen sulphide is called *sulphur water*. Ocean water contains 3.5% of solids. Nearly 2.7% is common salt.

68. Drinking Water. — The adjective "pure," as applied to water, means different things to different classes of people. To the *chemist* it means water free from all dissolved or suspended substances. To the manufacturer it means water suitable for use in boilers or as a cleanser on a com-

mercial scale. To the housekeeper it means water suitable for household *cleansing*, for *cooking*, and, above all, for *drinking*.

Drinking water should not contain more than .03 of 1% solid matter, and not more than $\frac{1}{15}$ of this should be organic. Decaying animal matter is the natural breeding place of disease-producing bacteria. To be good a water should not contain more than **traces** of it. The appearance of a water is no indication of its purity; a clear, cool, and pleasant water may be polluted, while an unattractive one may be harmless. A careful examination, called a "**Water Analysis**" is needed to determine the quality of a water. The analysis consists of a *chemical* examination for the non-living ingredients, and a *bacteriological* study of the microorganisms present. It should also include an *inspection of the surroundings* of the source of the water, to determine whether or not kitchen drains, outbuildings, or barns may be so situated as to pollute the water.

69. Purification of Water. — Drinking water may be purified (1) by **filtration**; (2) by **boiling**; (3) by **distillation**.

(1) **Filtration** of water consists in passing it through *porous* material. The filter not only "strains out" insoluble substances, but it assists in *oxidizing* organic impurities, by bringing them into intimate contact with air. A household filter may be a porous tube which is attached to the

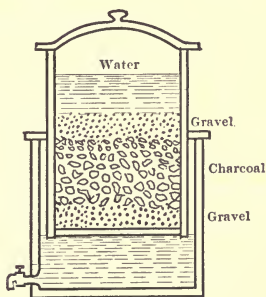


FIG. 26.

faucet, or it may be a jar with a porous bottom, with or without the gravel and charcoal shown in Fig. 26.

The water for an entire city is often filtered through layers of sand and gravel acres in extent and several feet deep. Tile drains at the bottom conduct the water to a reservoir. All filters should be cleaned frequently, or they themselves become sources of pollution. Aluminum salts are often used to purify water by **coagulation**. They react with the soluble substances present, producing a *precipitate* (cf. §§ 87 and 476), which carries down finely suspended clay particles and the germs clinging to them.

(2) **Boiling** the water kills the microorganisms present, and makes limestone insoluble by expelling the carbon dioxide (cf. §§ 67 and 284). The soluble substances remain. Since the taste of fresh water is due largely to the dissolved gases, boiling, *like distilling*, leaves the water "flat." Filtering the boiled or distilled water, or shaking it with air, restores the gases, and makes the water palatable and wholesome.

(3) **Distillation** consists in converting a liquid into vapor, and then condensing the vapor. All impurities more "volatile" than the water, such as ammonia, etc., appear in the first portions of the distillate; all less volatile remain in the still.

The distilling apparatus used in laboratories is shown in Fig. 27. The condenser is called a **Liebig's** condenser. It

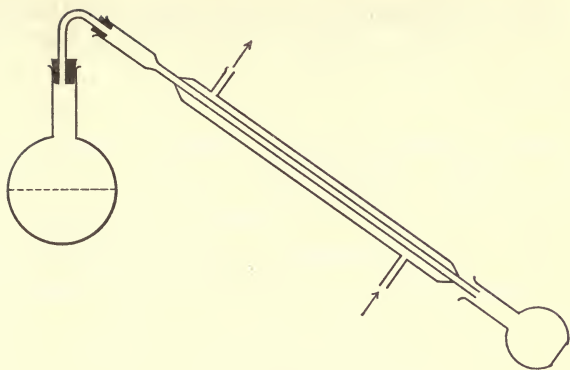


FIG. 27.

consists of an inner tube for condensing the vapor, and an outer jacket through which cold water is kept running.

Chemically pure water is hard to prepare and keep. Even water so pure that it will leave no residue when evaporated in a platinum dish cannot be kept pure long, for it acts upon the glass or porcelain vessels in which it is stored or used.

70. Hardness of Water. — Water that contains *gypsum*, *limestone*, *magnesium chloride*, etc., does not *wet* the skin readily, and is called “hard” water. Soap reacts with hard water, forming an insoluble “scum” (*cf.* § 413), and thus removes the hardness. Water is “soft” when it forms permanent suds with soap. The **hardness** of a water may thus be defined as its *soap-consuming* power. Hardness is of two degrees: temporary and permanent. Temporary hardness may be removed by boiling

(*cf.* § 284); permanent, only by using “softeners,” such as washing powders, lime, ammonia, etc. (*cf.* § 435).

71. Physical Properties of Water. — Pure water is practically odorless and tasteless. In small quantities it is colorless; in large masses, blue. Water is the only substance we deal with **commonly** in its three physical states of solid, liquid, and gas.

Ice melts at 0° C. under 760 mm. pressure. Water freezes at the same temperature, if it is in motion, or *if it is in contact with ice*. If kept perfectly quiet, it may remain liquid below 0° C., in a “superfused” condition (*cf.* § 86). When the supercooled liquid begins to freeze, its temperature rises to 0° C. On freezing, water *expands*; 10 c.c. become 10.9 c.c. of ice. The density of water is at its maximum at 4° C.; its relative density is then 1 (*cf.* § 6). The relative density of ice is 0.92.

When a gram of water freezes it gives off 79 *calories* of heat (*cf.* § 55). The same amount is needed to melt a gram of ice; the *heat of solidification* of water is equal to the *heat of fusion* of ice.

Water, even ice, evaporates at all temperatures. The vapor tension of each at 0° C. is 4.5 mm. At 100° C. the vapor tension of both water and steam is 760 mm.; at 150° C. it is 3,581 mm. The *boiling point* of a liquid is the temperature at which the pressure of its vapor equals that of the atmosphere

in contact with it; hence the boiling point of water is 100° C. under 760 mm. pressure.

Steam is a colorless gas, 9 times as heavy as hydrogen. One cubic centimeter of water gives about 1200 c.c. of steam. To convert 1 g. of water at 100° C. into steam at 100° C. requires 537 calories. This is the *heat of vaporization* of water. The *heat of condensation* of steam just equals it.

The **specific heat** of water (1) is high; more heat is needed to warm a given weight of water 1° C. than is needed for the same weight of any other substance except hydrogen (see Appendix iii). Water is a poor conductor of heat and of the electric current (*cf.* § 174).

72. Chemical Properties. — The chemical properties of water are given in detail in other sections. They are: —

(1) Water is very *stable* (§§ 60, 73, and 311), but it is decomposed by the electric current.

(2) It reacts with some metals to give basic *hydroxides* (or oxides) and *hydrogen* (*cf.* §§ 57 and 74).

(3) It reacts with certain *non-metals*, such as *chlorine* and *fluorine*, to give *acids* and oxygen (*cf.* §§ 119 and 317).

(4) Water unites with *oxides of metals* to give bases, and with oxides of *non-metals* to give acids (*cf.* §§ 161 and 162).

(5) Water unites with many compounds to form *hydrates* (*cf.* § 88, “water of crystallization”).

73. Dissociation of Water by Heat.

Above 1000° C. steam undergoes a slight decomposition into hydrogen and oxygen. The amount *increases as the temperature rises*, but at 2000° C. is only 1.8%. No matter how long steam is kept at 2000° C., the amount of the decomposition cannot be made greater, because the elements **recombine** as *rapidly as they are separated*. A decomposition like that of steam, in which there is *equilibrium* between decomposition and combination, is called a **dissociation**. Above 2000° C., the dissociation will be greater than 1.8%, but there will be equilibrium, as at 2000° C. If the temperature is lowered, enough hydrogen and oxygen recombine to produce equilibrium at the lower temperature.

74. Action of Metals upon Water. — We commonly apply the name “metal” to substances like iron, copper, silver, gold, etc. These are all fairly hard, heavy, malleable, and ductile (*cf.* § 8). They melt at a high temperature, and do not react rapidly with air or water, under ordinary conditions. The metals named in § 57 (2) differ from the common metals in many respects. They are light (*cf.* § 408, Table), soft (except *calcium*, which has the hardness of lead), and act so rapidly with ordinary air that they must be kept under kerosene or ligroin. They have a metallic luster when freshly cut, but this tarnishes quickly. They react rapidly with water, giving hydrogen and the hydroxide of the metal.

The action of sodium is typical. When a piece of it is thrown

upon water (this is done at arm's length, and a piece of glass is held between the face and the dish to avoid danger from spattering), the heat of the reaction melts the sodium, and the globule of metal swims about until used up. A lighted match brought near the sodium sets the escaping hydrogen on fire. The hydrogen may be collected by placing the sodium in a short piece (1 cm.) of glass tubing, and then plunging it quickly, by the use of tongs, under the mouth of an inverted bottle of water standing in a water-pan.

The dilute solution of sodium hydroxide formed by the reaction feels *soapy*, has a *bitter taste*, and turns red litmus *blue*. Evaporation of the water would leave the sodium hydroxide as a white solid (*cf.* § 412).

When **potassium** is put upon water, the heat of reaction *sets the hydrogen on fire*.

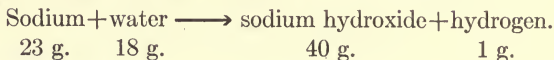
Calcium reacts with water more slowly than sodium, but gives corresponding products.

75. Weight Relations of the Reaction; Hydroxides.

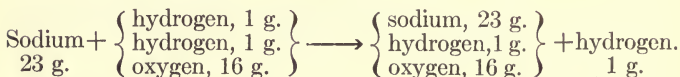
— If a known weight of sodium is added to water, and the hydrogen formed is collected, the relation by weight between the hydrogen and the sodium that displaced it can be readily determined. Experiment shows that it takes 23 grams of sodium to set free 1 gram of hydrogen. If 23 grams of sodium were actually added to water, and the excess of water were evaporated, the sodium hydroxide would weigh 40 grams. *If no new matter is produced by the reaction*, then the production of 40 g. of sodium hydroxide and 1 g. of hydrogen must require 18 grams of water in addition to the 23 grams of sodium:—

$$23 + 18 = 40 + 1.$$

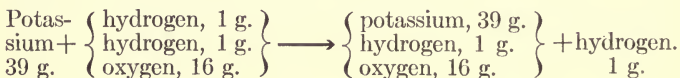
Experiment shows this is actually the case: —



Or we may write it thus: —

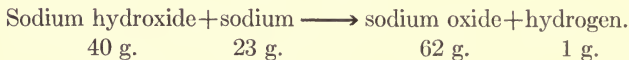


For **potassium** and water the weight relations are: —

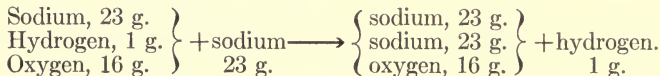


It is plain that *in both cases* the hydroxide contains **half** the hydrogen of the water used, the other half being set free. We may thus define a hydroxide as *water with half of its hydrogen replaced by a metal*.

By proper methods *sodium* may be made to react with *sodium hydroxide*; 23 grams of sodium again liberate 1 gram of hydrogen; this time from the sodium hydroxide, —



That the reaction is a replacement of hydrogen by sodium is more evident if we give details: —



76. Equivalent Weights. — In §§ 64 and 65 we learned that the Law of Definite Proportions applies to *combination of elements*; § 75 shows that it applies

also to the *replacement of one element by another*. Chemists use **two** sets of numbers to represent **equivalent amounts** of the elements, that is, to represent the proportions by weight in which the elements combine with, or replace, one another. One of these sets is called the **equivalent weights**; the other, the **atomic weights**. The atomic weights will be studied later (§ 152). They *depend upon* the equivalent weights, but are not identical with them.

The equivalent weight of an element is the weight of it, in grams, that combines with, or replaces, 8 grams of oxygen or 1 gram (more exactly, 1.008 g.) of hydrogen. The weights taken as standards are *equivalent to each other*, for they represent the proportions in which the two elements unite to form water.

The following table gives some of these weight relations in an easily scanned form:—

		HYDROGEN.	SODIUM.	POTASSIUM.	CHLORINE.	ZINC.	OXYGEN.
8 g. Oxygen	Are equivalent to	1.008 g.	23 g.	39 g.		32.7 g.	
1.008 g. Hydrogen			23 g.	39 g.	35.45 g.	32.7 g.	8 g.
23 g. Sodium		1.008 g.			35.45 g.		8 g.
39 g. Potassium		1.008 g.			35.45 g.		8 g.
35.45 g. Chlorine		1.008 g.	23 g.	39 g.		32.7 g.	
32.7 g. Zinc		1.008 g.			35.45 g.		8 g.

The equivalent weights are determined solely by accurate quantitative experiments. They depend upon no theory. To

get the equivalent weight of zinc, we treat a known weight of zinc with some acid, collect and get the weight of the hydrogen, and calculate the weight of zinc needed to produce 1.008 g. of hydrogen. Or we may convert the zinc into zinc oxide, and calculate how much zinc would have united with 8 g. of oxygen.

77. Exercises and Problems.

1. If 10 c.c. of hydrogen are mixed with 10 c.c. of oxygen, and the mixture is exploded in a eudiometer, which gas is left? How much of it? How much steam is formed?

2. When hydrogen was passed over some heated cupric oxide 1.89 g. water were formed, and the cupric oxide lost 1.678 g. Calculate the weight of oxygen combined with 1 gram of hydrogen.

3. In an experiment, 13.98 g. iron were dissolved in dilute sulphuric acid, and the hydrogen formed measured 5.6 liters under standard conditions. What is the equivalent weight of iron?

4. The equivalent weight of potassium is 39. How many grams of hydrogen are formed when 5 grams of it act upon water? How many grams of water are used up? How much potassium hydroxide is formed?

5. When 1.336 g. calcium reacted with water, 808 c.c. hydrogen were collected over water at 15° C. and 753 mm. Calculate the *equivalent weight* of calcium.

6. How would you determine the per cent of water in a potato?

7. What evidence is there that the hydrogen of water is more divisible than the oxygen?

8. For what units of measurement is water taken as a standard?

CHAPTER VI.

SOLUTION AND CRYSTALLIZATION.

78. Nature of Solution. — By solution, or dissolving, we generally mean the uniform mixing of a solid or gas with some liquid, called the **solvent**. The resulting mixture is called a solution. The dissolved substance is called the **solute**. Water, alcohol, and ether are common solvents. The solute imparts some of its properties, such as taste and color, to the solution, but its particles cannot be seen, and they will not settle when the solution stands. All true solutions are *clear*, whether colored or not. Particles that settle out on standing are said to be *suspended in* the liquid. While suspended they make the liquid *turbid*. Suspended materials can usually be filtered out; dissolved substances cannot.

The volume of a solution is greater than that of the solvent alone, but usually less than that of solvent and solute together. A considerable amount of powdered sugar may be added to a vessel apparently full of water without causing an overflow, while a much smaller quantity of an insoluble substance, such as sand, cannot.

79. Solubility. — By the *solubility* of a solute we

mean the **maximum** amount of it that can be taken up by a given quantity of solvent, *in the presence of an excess of the solute*. In the case of solids, solubility is expressed in the number of grams of solute for each 100 grams of solvent, at some definite temperature. Of course, any amount less than this maximum can be dissolved. *When no solvent is named, water is understood.*

By the **concentration** of a solution we mean the weight of solute actually present in a given quantity of solvent. A solution having a *small* concentration of solute is said to be **dilute**; one having a *large* concentration is said to be **concentrated**; one at *maximum* concentration, in the presence of an excess of the solute, is **saturated**.

SUBSTANCE.	GRAMS SOLUBLE IN 100 GRAMS WATER.		
	At 0° C.	At 20°.	At 100°.
Potassium nitrate.	13.3	31.7	246.
Sodium chloride.	35.	36.	39.7
Potassium chlorate.	3.3	7.2	59.5
Cupric sulphate.	15.5	22.	73.5

80. Conditions that Affect Solubility. — The conditions that affect solubility are called **solubility factors**. The chief solubility factors for solids and liquids are: —

- (1) Character of the *solute* itself.
- (2) Character of the *solvent*.
- (3) The *temperature* at which solubility is determined.

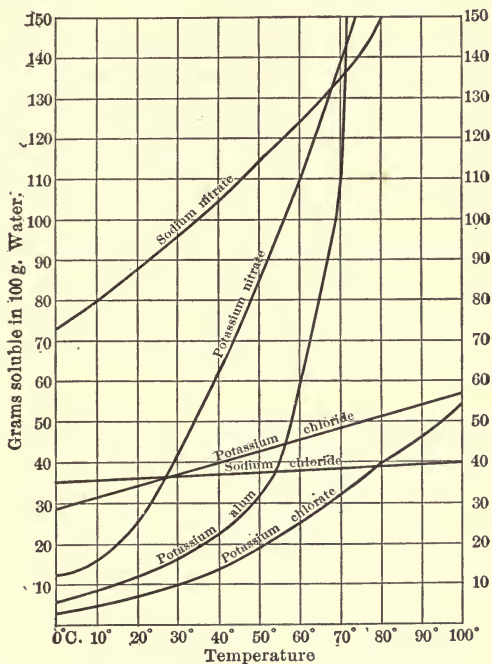


FIG 28. SOLUBILITY CURVES.

(1) The influence of the nature of the solute is shown clearly by the *table*, § 79, by Appendices vii and viii, and by the "Solubility Curves" (Fig. 28). A substance is *insoluble* only by comparison with other substances. There is probably *no substance without some solubility*. Both *strontium sulphate* and *barium sulphate* are called "insoluble," but while the former requires

8,000 times its own weight of water to dissolve it, the latter requires 400,000 times. A solid requiring less than 100 times its weight of solvent for solution is considered *readily* soluble; one needing between 100 and 1,000 times its weight, *difficultly* soluble; one needing more than 1,000 times its weight of solvent is called *insoluble*.

(2) The solubility of a substance in one solvent has no relation to its solubility in another. Thus, sugar and salt are very soluble in water but insoluble in ether. Water is the most common solvent for inorganic substances; alcohol is next. In pharmacy, an alcoholic solution is called a **tincture**. Alcohol and ether are the most common solvents for organic compounds.

(3) *Temperature as a solubility factor* is shown in the table and in the **Solubility Curves** (Fig. 28). The rapid increase of solubility with rise of temperature is usual with solids. Some, however, like salt, have almost the same solubility at 100° C., as at 0° C. Others, like calcium hydroxide and calcium sulphate, are less soluble in hot than in cold water.

81. Properties of Solutions. — Solutions of solids boil at a higher temperature and freeze at a lower temperature than the pure solvent. Thus a saturated solution of salt in water boils at about 109° at 760 mm., and freezes at -21° C. The rise of the boiling point and the lowering of the freezing point are smaller, of course, for less concentrated solutions. The specific gravity of solutions of solids is greater than that of the solvent. Thus, sea water has a specific gravity of 1.026.

82. Solubility of Liquids. — Liquids dissolve in other liquids, but we usually speak of the solution as a *mixing* of the liquids. Water and alcohol are

miscible in all proportions, but ether and water are *immiscible*. Of course the term "immiscible," like "insoluble" (*cf.* § 80), must not be taken literally. It means simply that the solubility of water in ether and of ether in water are small. After equal volumes have been shaken together, they separate again into two layers, the lighter, ether, on top (*cf.* Appendix v). Chloroform and water are also immiscible, but here water forms the upper layer.

83. Solubility of Gases. — Gases dissolve in liquids, just as solids and other liquids do, up to the point of saturation. The *factors of solubility* are the same as for solids and liquids, with the addition of **pressure**.

Difference of Solvent. — Under standard conditions 100 c.c. of water dissolve 2.1 c.c. hydrogen, while the same volume of alcohol, under the same conditions, dissolves 7 c.c. hydrogen.

Effect of Temperature. — Gases show a *decrease of solubility as the temperature rises*. Thus 100 c.c. of water dissolve 4.1 c.c. of oxygen at 0° C., 2.9 c.c. at 15°, 1.84 c.c. at 50°, and *none* at 100°. At the boiling point water usually gives up all dissolved gases. This is not true of *hydrogen chloride* (*cf.* § 127).

Solubility of Different Gases. — Gases may be divided into *two* classes according as they are.—

(1) *Very soluble*, or (2) *moderately soluble*. To the very soluble gases belong *ammonia*, *hydrogen chloride*, *sulphur dioxide*, etc. One c.c. of water, under standard conditions, dissolves 1146 c.c. of ammonia, 505 c.c. of hydrogen chloride, and 80 c.c. of sulphur dioxide. Solution, in such cases, is partly *union with water*.

Thus the solution of ammonia contains ammonium hydroxide (*cf.* § 209), and that of sulphur dioxide, sulphurous acid (*cf.* § 259).

To the moderately soluble gases belong oxygen, hydrogen, and nitrogen, of which 100 c.c. of water, under standard conditions, dissolve 4.1 c.c., 2.1 c.c., and 2 c.c. respectively.

Effect of Pressure upon Solubility. — The *solubility* of a gas in a given solvent, at constant temperature, is *proportional to the pressure*. This is **Henry's Law**. It applies to *moderately soluble* gases, not to such gases as ammonia, etc. Under standard conditions 180 c.c. of carbon dioxide dissolve in 100 c.c. water. If 100 c.c. of water are saturated with the gas at 0° C., under half an atmosphere pressure (380 mm.), and the gas is expelled and collected at 0° C. and 760 mm., its volume will be 90 c.c. Under two atmospheres, at 0° C., 360 c.c. of carbon dioxide dissolve.

84. Saturated and Supersaturated Solutions. —

There are two methods in common use for saturating a solution, at the ordinary temperature, with a solid. In the *first*, the solution is shaken or stirred with an **excess** of the solid until saturation is reached (*cf.* § 79). In the *second* method the solution is heated with enough solid to produce saturation at a *higher* temperature, and the solution is then cooled to the ordinary temperature. The excess of the solute usually crystallizes out.

If, however, none of the solid solute remained in contact with the solution, some solutes will not crystallize out on cooling, even though present in larger amount than necessary to saturate the solution. Such solutions are said to be **supersaturated**. Sodium chlorate, sulphate, and thiosulphate

("hypo") form supersaturated solutions. A *crystal of the solute* causes them to become saturated, the excess of solute being deposited. Jarring the solution, or introduction of dust particles, may cause a crystal of the solute to be formed (*cf.* § 71).

85. Energy Changes during Solution; Freezing Mixtures. — When a *gas* dissolves in a liquid, heat is generally liberated, but when a *solid* dissolves, heat is usually absorbed. Thus, when equal parts, by weight, of water and ammonium nitrate are mixed at 0° C. the temperature falls to -15° C. Some exceptions to the rule are given in § 88.

The energy that disappears when solids dissolve is used in changing them to the dissolved state. Salt and ice form our most common "*freezing mixture*." The temperature can be brought down to the freezing point of saturated brine (-21° C.). In the ice-salt mixture the temperature falls because heat is absorbed both in the dissolving of the salt and in the melting of the ice. The hydrate of calcium chloride (*cf.* § 433) and ice give a mixture freezing at about -40° C.

86. Crystallization. — Solids generally separate from solution in regular masses, called *crystals*. To crystallize a solid from solution, we commonly use method 2, of § 84, *i. e.*, we let the hot, saturated solution cool. Crystals may also be formed by slow evaporation of the solvent. *The more slowly crystallization takes place, the larger and more perfect the crystals.* Sometimes crystals are allowed to form

upon a string suspended in the solution, as in the case of "rock-candy."

Crystals are formed, not only from solution, but also by the *freezing* of a liquid. This is "crystallization from fusion." Thus, water, melted sulphur, and melted zinc, all solidify in crystalline form. When liquid water freezes, the ice crystals fit closely together, but when atmospheric water (*cf.* § 194) solidifies, in *snow* and *frost*, the crystal-masses are separate. A description of crystal forms is given in Appendix xi.

Just as some solutions remain "supersaturated" when cooled, so some liquids remain "superfused," that is, they do not solidify at the temperature at which the solid form melts. Crystallization is effected, as in the case of a supersaturated solution, by "inoculation" with a crystal of the solid. When a superfused liquid becomes solid, the temperature rises to the true melting point.

87. Precipitation and Effervescence. — When a hot, saturated solution is cooled *suddenly*, the solid that separates out will consist of *very small* crystals ("crystal-meal"), or it will be **amorphous**, i. e., non-crystalline. In either case it is called a **precipitate**. Precipitation is also brought about (1) by *adding* to a solution *a solvent* in which the solute is insoluble; or (2) by a *chemical reaction* in which a new, insoluble substance is formed.

When gases separate rapidly from solution, the solution is said to "**effervesce**." Thus, a mixture

of zinc and dilute sulphuric acid, evolving *hydrogen*, and "soda water," from which *carbon dioxide* is escaping, both *effervesce*.

88. Water of Crystallization, or of Hydration. —

By water of crystallization we mean the water with which some substances combine when they are crystallized from water. A substance containing water of crystallization is called a **hydrate**. The hydrate deprived of its crystal water gives the **anhydrous** substance. The loss of crystal water by a hydrate is accompanied by a loss of crystalline structure and by other changes in properties. Thus *blue vitriol*, a hydrate of cupric sulphate, is a blue, crystalline solid which loses water when heated. A white powder, *anhydrous* cupric sulphate, remains. The anhydrous substance has its **own crystalline form**. It cannot be crystallized from water, because the product is then the hydrate, *blue vitriol*. However, it dissolves in concentrated, hot sulphuric acid, and crystallizes out, on cooling, in white needles. By no means all crystalline substances contain crystal water; cane sugar, salt, etc., crystallize from water as *anhydrous* substances.

The union of water with an anhydrous substance is a *chemical reaction*, because, —

- (1) A new substance is formed;
- (2) There is an energy-change; generally heat is evolved;
- (3) The substances combine in definite proportions (*cf.* §§ 10, 65, and 108).

While most solids cause the temperature to fall when they dissolve in water (cf. § 85), some *anhydrous* substances, such as anhydrous cupric sulphate, sodium carbonate, and calcium chloride, dissolve with *rise of temperature*. This is due to the fact that they combine with some of the water. When the *hydrates* of these substances dissolve, heat is absorbed.

Decrepitation. — Water is often enclosed between crystals, and escapes *explosively* (as steam) when they are heated. This produces “*crackling*” or **decrepitation**. Examples of substances that decrepitate when heated are *common salt* and potassium sulphate.

89. Efflorescence and Deliquescence. — When a hydrate *loses its crystal water* on exposure to the air it is said to **effloresce**. Such a substance is “*washing-soda*,” a hydrate of sodium carbonate. Some anhydrous substances take up water from the air and form hydrates. If so much water is absorbed that the hydrate becomes *moist*, or dissolves, the substance is said to **deliquesce**. Anhydrous calcium chloride illustrates *deliquescence*. A substance that absorbs moisture from the air is said to be *hygroscopic*.

The crystal water of a hydrate escapes when its vapor pressure *exceeds* that of the water vapor of the air; in the case of a deliquescent substance, however, the water vapor of the air has the greater pressure. Blue vitriol holds its water of crystallization under ordinary conditions, but *effloresces* in dry air.

90. Drying Agents. — Substances used to remove *water vapor* from gases, or *dissolved water* from liquids, are called **drying**, or *dehydrating*, agents. Thus

calcium chloride was used to dry hydrogen (*cf.* § 49). It may also be used to remove dissolved water from ether. Similarly, anhydrous cupric sulphate will remove water from alcohol.

Quicklime, *i. e.*, *calcium oxide* (*cf.* § 431) is a dehydrating agent because it combines readily with water to give *slaked lime*, calcium hydroxide.

91. Exercises.

1. Would an underground water in contact with carbon dioxide dissolve more, or less, of the gas than if it were at the surface? Why? What would occur if such a water were brought to the surface?

2. Why is it that insoluble substances, *e. g.*, sand, "burnt alum," etc., have no taste?

3. How could you separate a mixture of salt, white sand, and iron filings so as to recover each?

4. Suggest a method of separating a mixture of potassium nitrate and sodium chloride so as to recover almost all of the nitrate. See "Solubility Curves," § 80.

5. Why does dry salt "snap" out of a dish when heated?

6. Calculate the per cent of potassium dichromate in a solution containing 15 g. of dichromate and 120 g. water.

7. When 20.4 g. of a saturated solution of a solid were evaporated to dryness, 5.4 g. of the solid remained. Calculate its solubility.

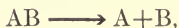
8. When 14.3 g. of a certain hydrate were heated, 9 g. of crystal water were lost. Calculate the per cent of loss. Calculate the volume of the steam formed at 150° C. and 720 mm.

CHAPTER VII.

FUNDAMENTAL LAWS AND THEORIES.

92. Classes of Reactions. — The fundamental fact regarding every chemical change is that at least one new substance is formed (§ 3). If the new substance is an element, it can have been formed only by the decomposition of a compound; if a compound, only by the decomposition of a more complex compound, or by the union of certain elements. Matter is not created or destroyed in a chemical change, but there is simply a *rearrangement* of elements. This is apparent when we classify chemical reactions. There are *four* classes: —

1. **Decomposition.** — Elements in combination become separated by a change of conditions, as when mercuric oxide is decomposed by heat into mercury and oxygen. Such reactions may be represented by the general expression, —



in which AB is the compound, and A and B are the parts into which it is broken up.

2. **Combination.** — Elements (or compounds) existing apart unite to form a (or another) compound. Thus, hydrogen and oxygen unite to form water. The general expression is —



3. **Replacement.** — In the common replacement reactions an element takes the place of one of the elements of a compound,

and the replaced element is set free. Thus, zinc and dilute sulphuric acid give zinc sulphate and hydrogen (§ 47). The general expression is —



4. **Double Decomposition.** — In this kind of reaction we have a concurrence of all the other three kinds. The general expression is —



To permit such an exchange of elements to take place, AB and CD must first be *decomposed*, and then *recombination* of their elements must take place *in a new way*. The final result is that A has *replaced* C, and D has replaced B.

An excellent illustration of double decomposition is the reaction of mercuric chloride with potassium iodide (*cf.* § 4). When these substances are *trituated*, *i. e.*, ground together, in a mortar, the products are mercuric iodide and potassium chloride. Another illustration is the reaction between solutions of lead chloride and potassium iodide. The products are *lead iodide*, which appears as a yellow precipitate, and potassium chloride, which remains in solution.

93. Conservation of Matter. — Since chemical changes are only rearrangements of elements, we understand why *the sum of the weights of the substances that react is always equal to the sum of the weights of the products*. This is the chemical form of the law of “**conservation of matter.**” It has proved true in every case that has been examined.

94. Law of Multiple Proportions. — The Law of Definite Proportions (§ 65) states that any given compound always contains the same elements united in the same proportion. A further fact must now be

considered, viz., that *the same two* (or more) *elements* may unite in **different** proportions to form *different compounds*.

Thus, hydrogen and oxygen form two distinct compounds, *water* and *hydrogen peroxide* (cf. § 339); carbon and oxygen form *carbon monoxide* (§ 286) and *carbon dioxide* (§ 276); carbon and hydrogen form *marsh gas* (§ 291), *ethylene*, and *acetylene*. The proportions, by weight, of the constituents of each are given in the following table: —

Water.	}	Ratio of hydro- gen to oxygen,	{	1 : 8.
Hydrogen peroxide.				1 : 16.
Carbon monoxide.	}	Ratio of carbon to oxygen,	{	3 : 4.
Carbon dioxide.				3 : 8.
Marsh gas.	}	Ratio of carbon to hydrogen,	{	3 : 1.
Ethylene.				6 : 1.
Acetylene.				12 : 1.

All of the cases named illustrate the **Law of Multiple Proportions**, which may be stated as follows: —

*If two elements form several compounds with each other, the different weights of one element which combine with a **fixed** weight of the other bear a simple ratio to one another.*

The law of multiple proportions was stated by John Dalton, in 1804, from the consideration of only a *few* compounds; but it has been confirmed by the work of the past century, and is one of the fundamental principles of Chemistry.

95. The Atomic Theory and the Law of Definite Proportions. — To explain the laws of definite and multiple proportions, Dalton devised the hypothesis

that matter is composed of **atoms**, or *indivisible particles*, that the atoms have weight, and that chemical combination consists in the union of atoms. All the atoms of any one element, he assumed, have the *same* weight; atoms of different elements will have *different* weights.

Suppose one atom of one element (let us call it A) unites with one atom of another element (B), and so on throughout the whole mass of the two elements; it is evident that if there is the *same number* of atoms of each kind, none of either kind will remain uncombined when the action is complete.

Let us suppose, further, that the atoms of B are *twice* as heavy as the atoms of A. Then, if the elements unite atom for atom, the resulting compound will necessarily contain the elements in the proportion of *one* part, by weight, of A to *two* parts, by weight, of B. Or, if we analyze the compound consisting of A and B united atom for atom, and find that it contains *one* part, by weight, of A to *two* parts of B, we must conclude that the atom of B is twice as heavy as the atom of A.

In the light of the atomic theory, therefore, chemical action *must* take place between *definite weights* of substances. The theory is thus an explanation of the law of definite proportions (*cf.* § 65).

96. Explanation of the Law of Multiple Proportions. — The atomic theory is the explanation not only of the law of definite proportions, but also of that of multiple proportions. For, if atoms are indivisible, elements that combine with one another in more than one proportion must do so in *some way* that will not require the dividing of an atom; that

is to say, the elements A and B must unite in the proportion of *one* atom of A to *one* of B, or *one* of A to *two* of B, or *one* of A to *three* of B, or *two* of A to *three* of B, etc.

Let us suppose, as in § 95, that the atom of B is twice as heavy as that of A; then, if A and B combine atom for atom, it is evident that the compound formed will contain the elements in the proportion of *one* part, by weight, of A to *two* parts of B; but if *one* atom of A unites with *two* atoms of B, the resulting compound will contain the elements in the proportion of *one* part, by weight, of A to *four* parts of B.

Thus, if we assume the atomic hypothesis, it follows that elements which combine with one another in more than one proportion *must* do so according to the *law of multiple proportions*.

97. Atomic Weights.—The atomic hypothesis “explains” the laws of definite and multiple proportions by the assumption that the atoms have definite *weights*. We have no means of finding their *actual* weights, but we can get some ideas regarding their *relative* weights. These are called the **atomic weights**. As we learned in § 76, the atomic weights are closely related to the *equivalent weights*. In some cases, as with *sodium*, *potassium*, *chlorine*, etc., the two weights have the same numerical value, but in other cases the equivalent weight must be multiplied by some integer to give the atomic weight. Thus, the equivalent weight of calcium is 20; its atomic weight, 40. But while the equivalent weight

can be determined *without any assumption*, except that of a standard, the atomic weight of an element can be selected only by the use of certain theories. The description of the methods of obtaining atomic weights is given in Chapter XIII. We may, however, use the atomic weights at once. They represent the proportions, by weight, in which the elements unite, just as the equivalent weights do, but they represent a great deal more; hence, they are used *in place of* the equivalent weights.

The following list contains the *approximate* atomic weights of some important elements. The complete list is given in Appendix iii.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	ELEMENT.	SYMBOL.	ATOMIC WEIGHT.
Aluminum.	Al.	27.	Manganese.	Mn.	55.
Barium.	Ba.	137.	Mercury.	Hg.	200.
Bromine.	Br.	80.	Nitrogen.	N.	14.
Calcium.	Ca.	40.	Oxygen.	O.	16.
Carbon.	C.	12.	Phosphorus.	P.	31.
Chlorine.	Cl.	35.5	Potassium.	K.	39.
Copper.	Cu.	63.	Silicon.	Si.	28.
Fluorine.	F.	19.	Silver.	Ag.	108.
Hydrogen.	H.	1.	Sodium.	Na.	23.
Iodine.	I.	127.	Strontium.	Sr.	87.
Iron.	Fe.	56.	Sulphur.	S.	32.
Lead.	Pb.	207.	Tin.	Sn.	118.
Magnesium.	Mg.	24.	Zinc.	Zn.	65.

98. Atoms and Molecules. — While chemists, following Dalton, hold the *atomic* theory, physicists

assume that matter is composed of *other* particles, called **molecules**. Only by some such assumption can they explain (for the present, at least) the properties of gases as expressed in the laws of Boyle and Charles (*cf.* §§ 38 and 40). We reconcile the *molecular hypothesis* with the atomic hypothesis by assuming that the molecules are usually more complex than the atoms; that they are, in fact, *composed of atoms*. Atoms are thus thought of as the smallest possible particles of the elements (see, however, § 441) that can take part in a chemical reaction, while the molecule is the *physical unit of matter*, *i. e.*, it is the smallest portion of any substance, simple or compound, *that can exist by itself*.

To illustrate: The physical properties of water are determined by the properties of the water *molecules*; it is only when we subject water to a *chemical* change that we *divide* the molecule. Then it is that the properties of the oxygen and hydrogen atoms come into play.

The molecules of *elements* consist of atoms of only *one* kind; while the molecules of *compound* substances contain atoms of *two or more* kinds.

99. Properties of Molecules.

Molecules are very small: Lord Kelvin estimates that 1 c.c. of a gas, under standard conditions, contains not less than 100 million million million of them (100,000,000,000,000,000,000). The distances *between the molecules* of gases are about 1,000 times as great as the diameters of the molecules. When gases are *compressed*, it is the distance between molecules that is made smaller, not the molecules themselves. By “distance

between molecules " we mean *average* distances, for molecules are not at rest, but *in motion*. *Molecular motion is heat*. The rapidity of the motion determines the *temperature*. The cause of the motion is the *inherent energy* of the molecules. The *direction* of the motion is along straight lines, except as the molecules collide with one another, or with the walls of the containing vessel. Molecules "occupy space" much as a person "occupies" a room, not by filling it completely, but by moving about in it.

100. The Molecular Theory and Physical State. —

The theory of molecules explains the differences between the gaseous, liquid, and solid states. The energy of the particles of a gas is so great that the gas "fills" any space presented to it, and exerts *pressure* upon the walls of a containing vessel. The attraction between molecules (*cohesion*) is slight in gases. Because of molecular motion, gases do not remain in layers according to their densities, but *mix in all proportions*, giving a mixture of uniform composition. The **air** is such a mixture (*cf.* § 200).

In the case of **liquids**, the cohesion between molecules is greater than with gases, yet the molecules move about freely enough to permit the liquid to take the form of the containing vessel. Because the molecular energy is less, diffusion is more slow than with gases, and the extent to which it can take place is often *limited*. Thus, ether dissolves in water, and water in ether, up to a certain limit (*cf.* § 82).

In **solids**, cohesion predominates, and the molecules do not usually alter their relative positions. As a result, a solid has a *definite form*. Molecular motion has not ceased, however, although solids diffuse into other solids very slowly. A case of

“solid diffusion” was the formation of the alloy, *solder* (cf. §§ 512 and 515), from its constituents *without melting*. The metals were subjected to a pressure of about 6,000 atmospheres, in steel molds, and *diffused into each other*, as gases do at ordinary pressure. The solder had the same properties as that made by melting the constituents together.

101. Exercises.

1. Give the origin and meaning of triturate, deliquesce, effloresce, conservation, marsh gas, atom, molecule, hypothesis, theory, cohesion, adhesion.

2. In which of the cases given in this chapter does an element have more than one equivalent weight?

3. What theory accounts for the effects of temperature and pressure upon the volumes of gases? How does this theory explain the evaporation of liquids? The dissolving of solids? Why, on the basis of this theory, must crystals be allowed to form slowly if they are to be large and perfect (cf. § 86)? Why do solids generally dissolve more readily in hot water than in cold, while gases do not?

4. Look up, in the Appendix, the atomic weights of sodium, potassium, chlorine, oxygen, hydrogen, carbon. Why are the figures somewhat different in the two columns?

CHAPTER VIII.

EQUATIONS AND NOMENCLATURE.

102. **Symbols, Formulas, and Equations.** — In place of the *names* of substances chemists use **symbols** and **formulas**. A *symbol* is a capital letter, or a capital and a small letter, that stands for an *element*. The letter used is the *initial letter* of the name of the element. When two names begin with the same letter a second letter is added to distinguish them. Thus the symbols C, Cl, and Ca stand for carbon, chlorine, and calcium respectively. Some symbols are derived from the Latin or Græek, *e. g.*, Hg for mercury.

A *compound* is represented by the symbols of its elements written side by side. The resulting expression is a **formula**. Thus HgO stands for *mercuric oxide*, and HCl for *hydrogen chloride*.

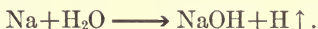
An **equation** stands for a *reaction*. It is made up of the symbols and formulas of the factors and the products (*cf.* § 5).

Thus, the equation for the reaction between sodium and water is, —



Na is the symbol of sodium (from *natrium*); H, that of hydrogen; O, that of oxygen. The formula H_2O , for *water*, shows that water is composed of hydrogen and oxygen; while the formula NaOH, for *sodium hydroxide*, shows that sodium hydroxide is

a compound of sodium, oxygen, and hydrogen. The sign $\longrightarrow$ is read "give," or "produce," and the sign $+$ is read "and." The equation is read *in the direction of the arrow*. Two arrows are generally used in an equation showing *replacement* or *double decomposition* (cf. § 92); one to show the direction in which the equation is to be read, and the other, what becomes of the products. The equation given above thus becomes, —

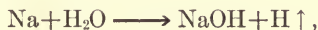


The arrow pointing *upward* indicates a gas; one pointing *downward*, a precipitate. When *nothing is removed*, as when the products formed by mixing two solutions are *soluble*, the **double arrow** is often used (cf. § 242).

103. Quantitative Meaning of Equations. — An equation stands for a reaction not only *qualitatively*, but **quantitatively**, that is, it represents not only what substances are taken and produced, but also their *proportions, by weight*. We give this quantitative meaning to the equation by letting the symbol represent not only the element in general, but also an **atom** of it. Then, since each element has a definite atomic weight, the symbol means, also, an **atomic weight** of the element. Finally, since our common unit of weight, in Chemistry, is the *gram*, the symbol is allowed to represent a **gram-atomic weight** of the element, *i. e.*, as many grams of it as there are units in its atomic weight. Thus, the symbol O stands for *oxygen*, for an atom of oxygen, for an *atomic weight* of oxygen, and for a **gram-atomic weight** of oxygen, *i. e.*, **16 grams**.

If the symbol represents the things named, for the atom, then the formula of a compound represents *corresponding* things for the molecule of the compound. The formula NaCl thus stands for a *molecule* of sodium chloride, a *molecular weight* of it (amounting to 58.5, the sum of the atomic weights 23 and 35.5), and a **gram-molecular weight** of it (58.5 grams), *i. e.*, as many grams of it as there are units in the molecular weight.

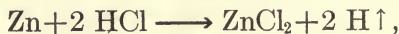
In accordance with these assumptions regarding symbols and formulas the equation, —



means that one *atom* of sodium reacts with one *molecule* of water to give one *molecule* of sodium hydroxide and one *atom* of hydrogen. If the symbols stand for *gram-atomic weights* (and they do), the equation also means that **23 grams** of sodium (see the list of atomic weights in § 97 and in the Appendix) react with **18 grams** (*i. e.*, 2+16) of water to give **40 grams** (*i. e.*, 23+16+1) of sodium hydroxide and **1 gram** of hydrogen. Of course the proportions will be just as true for pounds, tons, or milligrams as for grams.

104. Multiples of Symbols and Formulas. — In the formula for water (H_2O), the small numeral, **2**, after, and slightly below, the H, means *two atoms*, and *two atomic weights*, of hydrogen. A numeral so placed multiplies only the symbol immediately preceding it.

A figure before a formula multiplies every atomic weight in the formula. Thus, the equation, —



means that an atom of zinc reacts with two molecules of hydrochloric acid to give one molecule of zinc chloride and two atoms of hydrogen. It also means that 65 grams of zinc act upon 73 grams (*i. e.*, 2 [1+35.5]) of hydrochloric acid to give 136 grams (*i. e.*, 65+2×35.5) of zinc chloride and 2 grams of hydrogen.

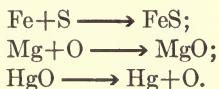
105. Radicals. — It often happens that a formula contains a *group* of elements repeated two or more times. Thus, the formula of calcium hydroxide is $\text{Ca}(\text{OH})_2$; it may also be written CaO_2H_2 ; or, better still, $\text{Ca} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$. In the first of these formulas, *viz.*,

$\text{Ca}(\text{OH})_2$, the small figure written after the parenthesis multiplies what is in the parenthesis immediately preceding, just as if the symbols in the parenthesis were together one symbol. Symbols which are grouped together in this way are called *radicals*.

Thus, all *hydroxides* contain the group **OH**. Sodium hydroxide is NaOH , and ferric hydroxide is $\text{Fe}(\text{OH})_3$. All *nitrates* have the radical **NO₃**, *e. g.*, NaNO_3 , $\text{Cu}(\text{NO}_3)_2$, and $\text{Fe}(\text{NO}_3)_3$. All *sulphates* contain the radical **SO₄**, *e. g.*, Na_2SO_4 , CaSO_4 , and $\text{Fe}_2(\text{SO}_4)_3$. The formulas of the cupric nitrate, $\text{Cu}(\text{NO}_3)_2$, and the ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, might be written CuN_2O_6 and $\text{Fe}_2\text{S}_3\text{O}_{12}$, respectively, but the first formulas are preferable

because they enable us to see that the compounds are derived from nitric acid and sulphuric acid, HNO_3 and H_2SO_4 , respectively, while the second formulas do not.

106. Writing Equations. — *Equations mean nothing unless they are the result of experiment.* If the student himself cannot prove what products are formed in a reaction, he must depend upon some trustworthy source, *e. g.*, the teacher or a text-book, for the information. When the factors and products are known, the equation may be written. Thus the union of iron and sulphur to form ferrous sulphide (*cf.* § 10), the burning of magnesium in oxygen (*cf.* § 24), and the decomposition of mercuric oxide by heat (*cf.* §§ 16 and 22) are represented by the equations,—



When sulphur is burned in air the product is *sulphur dioxide* (*cf.* § 257). The simplest equation would be,—



This equation is *qualitatively* correct; that is, it represents factors and products. It is not, however, **quantitatively** correct, for it shows *two* atomic weights of oxygen in the product, and only *one* as a factor. The correct *quantitative* equation is, —

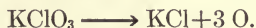


Changing the simplest equation into a quantitatively correct one is called "**balancing**" the equation. The three equations already given do not require balancing.

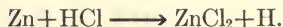
For the decomposition of potassium chlorate by heat (*cf.* § 19) the *simplest* equation is, —



The *balanced* equation is, —



The simplest equation for the action of hydrochloric acid upon zinc (*cf.* § 47) is, —



This equation cannot be balanced by changing the formula ZnCl_2 to ZnCl , for 65 parts of zinc unite with 71 parts of chlorine, as shown in the formula ZnCl_2 . The balanced equation is, —



107. To Represent Water of Crystallization. —

The water of crystallization present in a *hydrate* (*cf.* § 88) is represented by the formula of water (taken the necessary number of times) *after* the formula of the anhydrous substance. A period is placed between them. Thus, while CuSO_4 stands for *anhydrous* copper sulphate, blue vitriol, its **pentahydrate**, is $\text{CuSO}_4. 5 \text{H}_2\text{O}$. The zinc sulphate (*white vitriol*) obtained from water solution has the formula $\text{ZnSO}_4. 7 \text{H}_2\text{O}$, and Glauber's salt, the *decahydrate* of sodium sulphate, is $\text{Na}_2\text{SO}_4. 10 \text{H}_2\text{O}$.

108. Calculations from Formulas. — From the formula of a compound we can calculate the per cent

of each of the elements composing it. We get the atomic weights from the lists (§ 97 and Appendix). We calculate the percentage composition of water, H_2O , as follows:—

The hydrogen (2 gram-atomic weights) weighs 2×1 , or	2 g.
The oxygen (1 gram-atomic weight) weighs 1×16 , or	16 g.

The gram-molecular weight of water =	18 g.
--------------------------------------	-------

The hydrogen is $\frac{2}{18}$, or 11.11%.

The oxygen is $\frac{16}{18}$, or 88.89%.

In the same way we calculate the percentage composition of *aluminum oxide*, Al_2O_3 .

2 g. at. wts. of Al weigh 2×27 , or	54 g.
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3 g. at. wts. of O weigh 3×16 , or	48 g.
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Hence the gram-molecular weight of $\text{Al}_2\text{O}_3 = 102$ g.

Therefore the aluminum is $\frac{54}{102}$, or 52.94%,

And the oxygen is $\frac{48}{102}$, or 47.06%.

The *per cent of water of crystallization* may be calculated from the formula of the hydrate. Thus, from the formula of *blue vitriol*, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, we calculate as follows:—

1 g. at. wt. of Cu weighs	63 g.
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1 g. at. wt. of S weighs	32 g.
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4 g. at. wts. of O weigh 4×16 , or	64 g.
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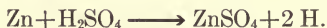
The gram-molecular wt. of <i>anhydrous</i> cupric sulphate is	159 g.
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5 gram-molecular weights of water weigh 5×18 , or	90 g.
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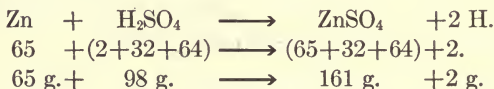
The gram-molecular weight of blue vitriol is	249 g.
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Therefore the water of crystallization is $\frac{90}{249}$, or 36.14%.

109. Calculations from Equations. — From the equation for a reaction we can calculate the proportions, by weight, in which the factors must be present, and the relative amounts of the products. Thus, the equation for the preparation of hydrogen from zinc and dilute sulphuric acid (*cf.* § 47) is, —



The proportions by weight may be written under the symbols and formulas: —



According to this equation, 65 grams of zinc react with 98 grams of sulphuric acid to give 161 grams of zinc sulphate and 2 grams of hydrogen.

Suppose, now, we wish to know *how much sulphuric acid is needed to react exactly with 40 grams of zinc.*

Solution. Since 65 grams of zinc require 98 grams of sulphuric acid for complete action (see equation), 40 grams of zinc will require $\frac{40}{65} \times 98$, or 60 grams of sulphuric acid. This is, of course, the *least* quantity of sulphuric acid that will use up all of the zinc. If a larger amount is used, the excess will simply remain in the solution.

The quantity of **zinc sulphate** formed may also be calculated, for if 65 grams of zinc give 161 grams of zinc sulphate, then 40 grams of zinc will give $\frac{40}{65} \times 161$, or 99 grams of zinc sulphate.

The *amount of the hydrogen* produced is, evidently, $\frac{40}{65} \times 2$, or 1.2 grams.

If we wish to find the weight of zinc needed to produce 5 grams of hydrogen, we solve as follows: —

Two grams of hydrogen are produced for every 65 grams of zinc used up, hence to produce 5 grams of hydrogen will require $\frac{5}{2} \times 65$, or 162.5 grams, of zinc.

Suppose the problem is: — “How much zinc is required to produce, by its action with dilute sulphuric acid, 40 liters of hydrogen at 0° C. and under 760 mm. pressure?”

We must first find the **weight** of the hydrogen, and then calculate the weight of the zinc necessary.

The weight of 40 liters of hydrogen under the conditions given is 40×0.09 , or 3.6 grams. Since 65 grams of zinc produce 2 grams of hydrogen, the weight of zinc needed to yield 3.6 grams of hydrogen is $\frac{3.6}{2} \times 65$, or 117 grams. If the volume of the hydrogen were measured at some other temperature and pressure, the first operation would be to reduce the volume (*cf.* § 44) to standard conditions, for the weight of a liter (0.09 gram) applies only under standard conditions.

110. How a Compound of Two Elements is Named.

— Most of the compounds we deal with have *two* or *three* elements. We call those having only *two*, **binary** compounds; those having *three*, **ternary** compounds. *The name of a binary compound contains the names of both its elements*, but the last syllable of one of them is changed to **ide**.

Thus *sodium chloride* is a compound of sodium and chlorine; *magnesium oxide*, one of magnesium and oxygen (here the *y* before the *ide* is omitted); *calcium carbide*, one of calcium and carbon; *lead sulphide*, one of lead and sulphur.

Most binary compounds contain a *metal* and a *non-metal* (*cf.* § 8), and it is the ending of the **non-metal** that is changed to *ide*. For purposes of

nomenclature, hydrogen is usually considered a metal, as in *hydrogen sulphide* and *hydrogen phosphide*. But its compounds with metals are called *hydrides*. All binary compounds of oxygen are *oxides*.

III. Naming of Different Compounds of the Same Two Elements. — If there are *two* compounds of the same two elements we distinguish between them as follows: —

(1) We change the final syllable of the name of the *first* element to **ous** or **ic**; or

(2) We place a prefix, usually a numeral or *per*, before the name of the **second** element.

The ending **ic** is given to the *first* element in the case of the compound having the *larger* proportion of the **second** element. The ending **ous** is used in the compound having the *smaller* proportion of the second element. Thus, the two chlorides of mercury, HgCl and HgCl_2 , are called *mercurous chloride* and *mercuric chloride*, respectively.

For some elements, *e. g.*, *copper* and *iron*, the Latin names are used. Thus we have the names *cuprous oxide* and *ferrous chloride* for the compounds having the smaller proportion of non-metal, and *cupric oxide* and *ferric chloride* for the compounds having the larger proportion of non-metal.

The **second method** of naming binary compounds is to use a numeral prefix *before* the second element. Thus, we have the names *carbon monoxide* and *carbon dioxide* for the substances CO and CO_2 ,

respectively, and the names *sulphur dioxide* and *sulphur trioxide*, for the compounds SO_2 and SO_3 , respectively.

112. Exercises.

1. What advantages can you see in using the formulas NaCl , H_2O , PbS , and NaOH , for the substances salt, water, galena, and caustic soda, respectively? How does the equation for the reaction between sodium and water (§ 102) show that "chemical action consists in changes in the relations of elements" (§ 92)?

2. Give the origin and meaning of the terms symbol, formula, equation, qualitative, quantitative.

3. Give the source of the symbols for sodium, potassium, mercury, iron, copper, silver, gold, lead.

4. What are the molecular weights of the following: Carbon monoxide, carbon dioxide, sulphur dioxide, alcohol ($\text{C}_2\text{H}_6\text{O}$), glycerine ($\text{C}_3\text{H}_8\text{O}_3$), and potassium chlorate?

5. Calculate the percentage composition of the following: Carbon dioxide, alcohol, potassium chlorate, sulphuric acid, sodium hydroxide.

6. If the equation for the reaction between magnesium and dilute sulphuric acid is $\text{Mg} + \text{H}_2\text{SO}_4 \longrightarrow \text{MgSO}_4 + 2 \text{H} \uparrow$, calculate how much hydrogen can be obtained if 10 grams of magnesium are used. How much magnesium sulphate? How much sulphuric acid is necessary?

7. Calculate the per cent of water of crystallization in Glauber's salt, white vitriol, and in gypsum, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$.

8. How many grams of phosphorus must be burned to produce 60 grams of phosphorus pentoxide, P_2O_5 ?

9. Name the compounds having the formulas CO , PbO_2 , SrCl_2 , SnCl_4 , HgI , HgI_2 , and BaC_2 .

CHAPTER IX.

CHLORINE.

113. Occurrence. — Chlorine is a heavy, greenish-yellow gas, of irritating odor and poisonous properties. It was discovered by the Swedish chemist Scheele in 1774, but was not generally considered to be an element until 1809.

Because of its great *reactivity*, i. e., its tendency to act chemically with other substances, chlorine is not found in nature *free*, but always in combination with other elements. Its most abundant compounds are sodium, potassium, and magnesium chlorides and hydrochloric acid, which is hydrogen chloride. Sodium chloride is common salt.

114. Common Method of Preparation. — Chlorine is usually prepared by the action of reagent hydrochloric acid upon manganese dioxide. The apparatus is shown in Fig. 29.

A flask containing manganese dioxide (MnO_2) in small lumps is provided with a thistle tube and a delivery tube, and is supported so that it may be warmed in a water bath. Concentrated hydrochloric acid is added through the thistle tube, and the evolution of chlorine begins. The gas is allowed to pass through a drying bottle one-third full of concentrated sulphuric acid (a U-tube of calcium chloride may be used instead), and then

into a collecting bottle, the air of which is to be displaced by chlorine. From the collecting bottle a delivery tube reaches beneath the surface of a solution of sodium hydroxide, which absorbs any escaping chlorine. When the gas is completely soluble in sodium hydroxide we know that the air in the apparatus has been displaced. When a collecting bottle is full of chlorine it is removed and stoppered, and replaced by another bottle until enough gas has been obtained. The evolution of chlorine is stopped by filling the flask with cold water.

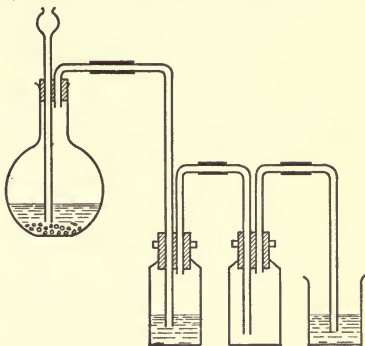
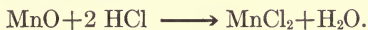


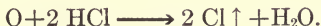
FIG. 29.

115. Study of the Reaction.

The reaction between manganese dioxide and hydrochloric acid is more complex than the reactions hitherto studied. The manganese dioxide reacts like *manganous oxide* and *oxygen* ($\text{MnO} + \text{O}$). If manganous oxide were to react with hydrochloric acid, a *double decomposition* would occur (*cf.* § 92) giving *manganous chloride* and *water*: —



Oxygen, alone, reacts with hydrochloric acid, giving water and chlorine: —



The *complete reaction* would, therefore, be represented by *adding the equations for the partial reactions*: —



Since the oxygen is not *actually* formed, it is best to enclose its symbol in a **parenthesis**. This indicates that it is an *intermediate product*. The partial equations thus become: —



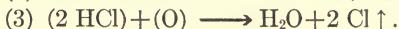
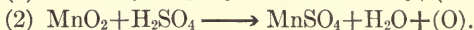
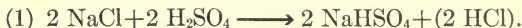
When the intermediate product (O) is eliminated, the sum of these partial equations is, as before, —



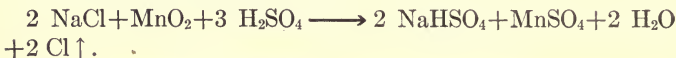
The *second* of the partial equations shows us that the *chlorine is formed by the oxidation of hydrochloric acid*.

For another view of the reaction, see § 138.

Instead of manganese dioxide and hydrochloric acid we may use *common salt*, manganese dioxide, and sulphuric acid. The reaction is practically the same, however, for the salt reacts with the sulphuric acid to give hydrochloric acid (*cf.* § 126), and this reacts with the manganese dioxide. The **stages of the reaction** are shown in the following *partial* equations:



The **complete equation** is, —

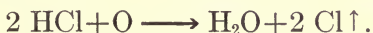


116. Other Methods. — Manganese dioxide is not the only substance that will liberate chlorine from hydrochloric acid; *potassium dichromate*, $\text{K}_2\text{Cr}_2\text{O}_7$; *potassium chlorate*, KClO_3 ; *nitric acid*, HNO_3 , *potassium permanganate*, KMnO_4 , and many other substances will do it.

But potassium chlorate and hydrochloric acid give, besides chlorine, an explosive oxide of chlorine. Similarly the chlorine formed from the action of nitric acid upon hydrochloric acid is mixed with other substances. Hence these methods are not used to prepare gaseous chlorine.

The mixture of nitric and hydrochloric acids is used extensively, however, under the name **aqua regia** (*i. e.*, royal water) as a solvent for gold, platinum, and other metals not readily attacked by single acids. *Aqua regia* — called, also, nitro-hydrochloric acid — *is thus only a source of chlorine*. Metals dissolved in it are converted into **chlorides**.

It will be noticed that the substances which react with hydrochloric acid to give chlorine are all *oxidizing agents*. The liberation of chlorine in all the methods described is thus brought about in practically one way, namely, by the *oxidation of the hydrogen* of hydrochloric acid to water, the chlorine being set free.



In **Deacon's Process** crude chlorine is made on a large scale by the use of atmospheric oxygen as oxidizing agent. Hydrogen chloride mixed with air is passed over heated bricks which have been soaked in copper sulphate or copper chloride solution. In the presence of these *catalytic agents* the oxygen of the air acts like the oxidizing agents named above.

The Electrolytic Method of making chlorine consists in *electrolyzing a concentrated solution of hydro-*

chloric acid or of sodium chloride. The chlorine, which is *electro-negative*, appears at the positive electrode, and the metal or hydrogen at the negative electrode (*cf.* § 61).

117. Physical Properties. — Chlorine is about $2\frac{1}{2}$ times as heavy as air, and 35.5 times as heavy as hydrogen. It is easily soluble in water, more than two volumes of the gas being absorbed by one of water at the ordinary temperature. The solution — called *chlorine water* — possesses many of the properties of the gas.

In a warm, saturated solution of common salt, chlorine is only slightly soluble; it may, therefore, be collected over brine instead of under air.

If chlorine is passed into iced water and the solution is cooled below 0° C., a crystalline substance separates out; this is a compound containing 144 parts of water to 71 of chlorine, and therefore represented by the formula $\text{Cl}_2 \cdot 8 \text{H}_2\text{O}$. It is called **chlorine hydrate**. Use may be made of this substance *to condense chlorine to the liquid state*.

For this purpose, the crystals of chlorine hydrate are dried between filter papers or on unglazed clay plates, and then put into the closed limb of a tube bent as shown in Fig. 30. The open end is then sealed. The end of the tube containing the chlorine hydrate is now warmed in a water

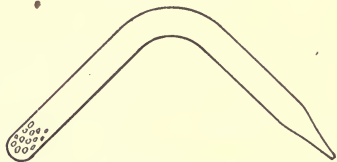


FIG. 30.

bath to 30° C., while the other end is surrounded by a freezing mixture of ice and salt. After a short time, liquid chlorine will condense at the drawn-out end. The gas has been liquefied by its own pressure. This experiment can be carried out only in a strong tube securely sealed.

Liquid chlorine is an article of commerce; it is stored and transported in iron cylinders.

118. Chemical Properties. — Chlorine is a very dangerous substance to inhale, and should, therefore, be generated only in a gas chamber, or where there is a good draught. If it has been taken into the lungs, alcohol or ammonia should be inhaled to counteract it.

It is always well to sprinkle a little ammonia water about in the neighborhood of a chlorine generator.

Chlorine is intensely active toward many other elements, forming, by direct union with them, the *chlorides*. Many substances that combine with oxygen slowly, or not at all at ordinary temperatures, unite readily with chlorine. Powdered antimony and copper foil (the latter must be hot) *glow* when put into chlorine, the products being antimony trichloride (SbCl_3) and cupric chloride (CuCl_2) respectively. Sodium, tin, magnesium, and phosphorus all give corresponding *chlorides* when put into the gas. But it is toward hydrogen that chlorine shows its most remarkable behavior, for while the two gases do not combine at all in the dark, and

only very slowly in diffused light, yet they unite with *explosive violence* in sunlight.

The mixture of hydrogen and chlorine may also be exploded by a burning match or by the electric spark.

Chlorine shows this tendency to combine with hydrogen not only when the hydrogen is in the free state, but also when it is united with other elements. As illustrations we may take the action of chlorine toward water, ammonia, and turpentine.

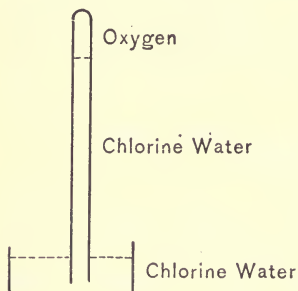
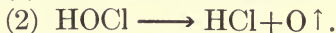
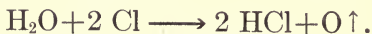


FIG. 31.

119. Action of Chlorine and Water. — The aqueous solution of chlorine may be preserved for a long time if kept cold and in the dark, but it decomposes rapidly in sunlight, giving as *final* products hydrochloric acid and oxygen. The stages of the reaction are: —

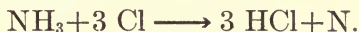


The complete reaction is, —



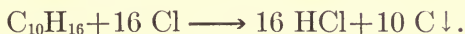
If the decomposition is carried out in a long tube (Fig. 31), oxygen will collect in the upper part of the tube.

120. Action of Chlorine and Ammonia. — When the hydrogen of ammonia is appropriated by chlorine, hydrochloric acid and nitrogen are formed, as represented by the equation, —



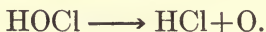
With the excess of ammonia the hydrochloric acid gives *ammonium chloride*, NH_4Cl , the material of the white smoke seen when ammonia and chlorine gases come together.

121. Action of Chlorine and Hydrocarbons. — The behavior of chlorine and hydrocarbons may be shown by immersing a piece of filter paper in warm turpentine and then plunging it into a jar of chlorine. The turpentine soon ignites, and burns with a smoky flame. The chlorine unites with the hydrogen, and sets carbon free.



122. Uses of Chlorine. — Chlorine is used in large quantities as a **bleaching** and **disinfecting agent**. It is not used *directly*, but is converted into *bleaching powder*, or “chloride of lime.” Bleaching powder is formed by the action of chlorine upon “slaked” lime (calcium hydroxide), and is easily decomposed by acids, even by the carbon dioxide of the air, with the formation of *hypochlorous acid*, HOCl (cf. § 329).

This is decomposed readily, giving *oxygen in an exceedingly active (nascent) condition.*



Fabrics to be bleached are, therefore, immersed alternately in baths of dilute acid and of chloride of lime. In this way *oxygen is set free in immediate contact with the coloring matter of the cloth, and bleaches it.*

Chlorine is not a bleaching agent ordinarily, unless water is present. The bleaching action of chlorine water, like that of bleaching powder, is due to hypochlorous acid (*cf.* § 119) and oxygen.

Compared with the old bleaching process, which consisted in exposing the fabric to the oxidizing agents of the air, the chlorine method is of course very rapid, but, unfortunately, the bleaching agent used too often attacks the fiber of the cloth as well as its coloring matter. Hence delicate materials, such as the better grades of straws, laces, silks, and woollens, are usually decolorized by *sulphur dioxide*, which, although it does not bleach so permanently, has yet the advantage of acting less upon the fabric.

The action of chloride of lime as a disinfectant is similar to its action as a bleaching agent: *nascent oxygen* is formed, and this destroys the micro-organisms of the surrounding air.

123. Nascent State. We have just seen that oxygen, as set free from bleaching powder and from chlorine water, is very active, and able to effect changes impossible under ordinary conditions. We say it is in a **nascent state**. The nascent condition is due either to the presence of *catalytic agents*, in contact with which the active element is liberated,

or to the **energy** given off when it is set free (*cf.* §§ 27 and 312).

124. Exercises.

1. How many grams of chlorine can, theoretically, be obtained by the electrolysis of 50 grams of hydrochloric acid?

2. How many grams of manganese dioxide are required to give with an excess of hydrochloric acid 10 grams chlorine?

3. How many liters of chlorine are needed, at 30° C. and 760 mm., to convert 12 grams of phosphorus into the chloride, PCl_3 ?

4. How much silver chloride, AgCl , can be formed by burning 54 grams silver in chlorine gas?

5. Calculate the per cent of chlorine in sodium chloride.

6. How many liters of chlorine can be made by the action of 25 grams of manganese dioxide with an excess of hydrochloric acid? (Assume that 1 liter of chlorine weighs 3 grams.)

CHAPTER X.

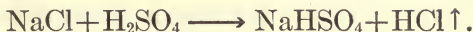
HYDROGEN CHLORIDE AND HYDROCHLORIC ACID.

125. Occurrence. — Hydrogen chloride is a colorless, heavy gas that fumes in moist air, and dissolves readily in water. It is found in only small amounts in nature, *e. g.*, in volcanic gases and in some springs. It makes up about 0.22 of 1% of the gastric juice. The aqueous solution is **hydrochloric acid**, or "*muriatic*" acid.

126. Preparation. (a) **Common Laboratory Method.** — Hydrogen chloride may be made by the action of sulphuric acid, H_2SO_4 , upon common salt, NaCl . The apparatus is like that for chlorine (Fig. 29).

The flask contains salt and sulphuric acid diluted with half its volume of water, and cooled. (**Caution!** *In diluting sulphuric acid always pour the acid into the water.*) A small flame or hot-water bath is used to heat the flask. The first bottle contains concentrated sulphuric acid to dry the gas, and the second bottle is for collecting it. A beaker of water collects any gas that would escape. When the gas bubbles in the beaker are *completely soluble*, we know that the collecting bottle is free from air.

The equation for the reaction is, —



(b) **Commercial Manufacture.** — On a commercial scale hydrogen chloride is made in a retort like that shown in Fig. 32. The “pan” is of cast-iron, about 10 feet in diameter, and inclosed in brick. There is a furnace below it, and a side door through which

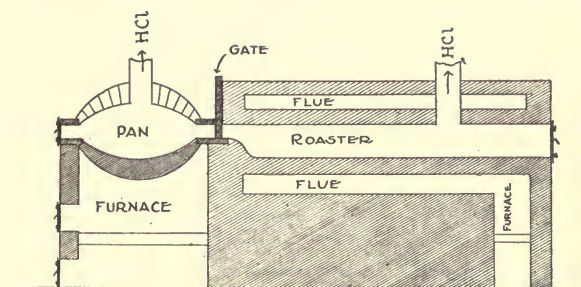
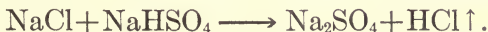


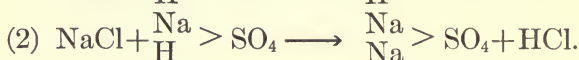
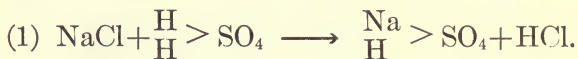
FIG. 32.

the “charge” can be put in. The charge consists of a ton or more of salt, and the amount of sulphuric acid necessary to produce sodium sulphate, Na_2SO_4 . The first stage of the reaction is shown in the equation given in (a). The hydrogen chloride is conducted off into water, forming commercial hydrochloric acid. When the mass in the “pan” is pasty it is raked over into the “roaster,” where it is heated to red heat. The second stage of the reaction then takes place: —



The sodium sulphate is used in the manufacture of glass, etc. (*cf.* § 418). Hydrogen chloride is also a by-product in the manufacture of soda (§ 414) by the Le Blanc process.

It is evident that *the hydrogen of sulphuric acid*, like that of water, *may be replaced in two stages*; for while at low temperatures only 58.5 grams of sodium chloride react with 98 grams of sulphuric acid, at a high temperature a *second* quantity of sodium chloride, equal to the first, is able to react, and thus produces a second quantity of hydrogen chloride. This will be more evident when the two equations are written together: —



127. Physical Properties. — Hydrogen chloride is about $1\frac{1}{4}$ times as heavy as air, and $18\frac{1}{4}$ times as heavy as hydrogen. It is very soluble, 505 c.c. being held by 1 c.c. water at 0° C. and 760 mm. pressure. The concentrated solution of the pure gas in distilled water at the ordinary temperature is the “*chemically pure*” (c. p.) **reagent** hydrochloric acid. This is a colorless liquid of specific gravity 1.2, which *fumes* strongly in moist air because the escaping gas condenses the water-vapor.

An aqueous solution of hydrogen chloride gives off the gas, if *concentrated*, or water, if *dilute*, until

the concentration is 20.2% of hydrogen chloride. Then it distills at 110° C.

The dry gas can be converted into a colorless liquid at a low temperature and great pressure.

128. Volumetric Composition of Hydrogen Chloride. — The composition of hydrogen chloride may be demonstrated in the same way as that of water, viz., by **electrolysis**. If an electric current of sufficient strength is passed through a concentrated aqueous solution of the acid, hydrogen is produced at the — electrode, and chlorine at the + electrode.

The gases collect at unequal rates, at first, because of the greater solubility of the chlorine; but when the liquid has become saturated with both gases the hydrogen and the chlorine gather in the collecting tubes at the same rate. See Fig. 33.

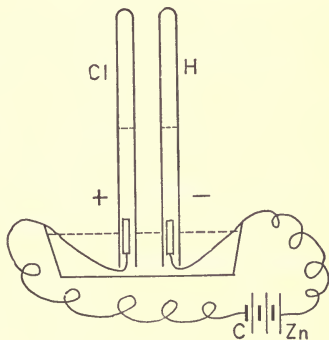
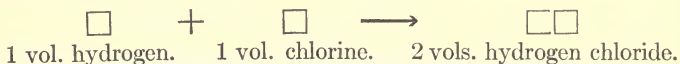


FIG. 33.

Therefore, hydrogen chloride must be composed of hydrogen and chlorine *united in equal proportions by volume*.

The same fact may be proved **synthetically**, for if a mixture of hydrogen and chlorine be exploded, it will be found that equal volumes of the two gases

have disappeared. The volume of hydrogen chloride formed will be equal to the sum of the uniting gases. These facts may be represented graphically as follows: —



Note that this case is different from that of water; for, in the production of 2 volumes of steam, 2 volumes of hydrogen united with 1 of oxygen, *i. e.*, 3 volumes of the mixed gases, gave only 2 volumes of the product.

Since the weights of equal volumes of hydrogen and chlorine are about as 1 : 35.5, the two volumes of hydrogen chloride formed by their union should be about 36.5 times as heavy as *one* volume of hydrogen. Hence hydrogen chloride should be about 18.25 ($=36.5 \div 2$) times as heavy as hydrogen. This is actually the case.

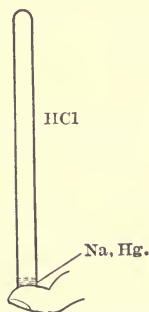


FIG. 34.

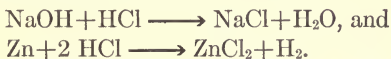
That hydrogen chloride gives, when decomposed, one-half of its own volume of hydrogen, may be shown by the action of sodium. For convenience the sodium is diluted by *alloying* it with mercury.

A small amount of the resulting *sodium amalgam* is put into a long measuring tube (Fig. 34) full of hydrogen chloride. The open end of the tube is then closed with the thumb, and the tube is shaken vigorously. When the thumb is removed under water, some of the water rushes up into the tube to replace the

chlorine. If the water inside and outside the tube is now brought to the same level, the volume of the residual hydrogen will be found to be approximately *one-half* that of the hydrogen chloride taken.

129. Chemical Properties. — When 1 gram of hydrogen unites with chlorine the heat liberated is 22,000 calories, consequently hydrogen chloride is very stable (*cf.* § 27). It does not react with most non-metals, but is oxidized by the air in the presence of catalyzers (*cf.* § 116), giving chlorine. The moist gas and its water solution are **acids**. Acids may be described roughly as having a *sour* (acid) *taste*, the ability to change certain vegetable colors, e. g., *blue* or *purple* litmus to *red*, and also the power to *neutralize* the properties of another class of substances, viz., the **bases**. Thus the action of hydrochloric acid upon *sodium hydroxide* (a base) gives *sodium chloride* (common salt) and water. *Metals*, too, react with acids, forming **salts**. Thus, zinc with hydrochloric acid gives zinc chloride (a *salt*) and hydrogen.

These reactions are shown in the equations, —



Hydrochloric acid is one of the most important acids. It is made on a large scale, and is used in enormous quantities to prepare chlorine and chlorides.

130. Chlorides.— The *chlorides* may all be considered *hydrogen chloride with its hydrogen replaced by a metal*. The most important chlorides have been given in § 113; others are *barium chloride*, BaCl_2 , *silver chloride*, AgCl , and *ferric chloride*, FeCl_3 . The most abundant chloride is, of course, *common salt*, NaCl .

The chlorides of most of the common metals are soluble in water. Exceptions are *silver chloride*, AgCl , and *mercurous chloride*, HgCl . *Lead chloride*, PbCl_2 , is only slightly soluble in cold water, but more readily in hot water.

When, therefore, solutions of salts of silver, lead, and mercury (in its mercurous condition) are treated with a solution of a chloride, the chlorides of these metals are *precipitated*.

131. Exercises.

1. 300 c.c. of hydrogen and 250 c.c. of chlorine were mixed and exploded. What was the product? Its volume? Which of the gases used was in excess? How much?

2. Calculate the percentage composition of hydrochloric acid.

3. How many grams of sodium chloride are needed to yield, with sulphuric acid, 20 grams hydrogen chloride?

4. How many grams hydrogen chloride can be made from 35 grams potassium chloride, KCl ?

5. What weight of sodium chloride is necessary to produce, with sulphuric acid, 20 liters of hydrogen chloride at -20°C . and 800 mm. pressure?

6. How many liters of hydrogen chloride can be made, at 40°C . and 650 mm., by heating 117 grams of salt to red heat with an excess of sodium hydrogen sulphate?

CHAPTER XI.

VALENCE.

132. Meaning of Valence. — The formulas of the chlorides (Chapters IX and X) show important differences. While in *sodium chloride* (NaCl) each sodium atom is combined with *one* chlorine atom, in *calcium chloride* (CaCl_2) one atom of calcium holds **two** atoms of chlorine. In *antimony chloride* (SbCl_3) the relation is 1 to 3, and in *platinum chloride* (PtCl_4) it is 1 to 4. Similar differences appear in hydrogen compounds, —

Hydrogen chloride, ClH ;
Water, OH_2 ;
Ammonia (§ 203), NH_3 ;
Marsh gas (§ 291), CH_4 .

*This ability of the atoms to unite with different numbers of other atoms is called **valence**.*

133. Standard of Valence. — The direct measure of the valence of an element in any compound is the number of hydrogen atoms with which one atom of the element combines. Since the hydrogen atom is *never* found in combination with more than one atom of another element, it is said to have a **valence of 1**, or to be *univalent*. The valence of *chlorine* in

the chlorides is, likewise, 1. In water, the *two* hydrogen atoms, with a total valence of 2, hold **one** atom of oxygen. The valence of the oxygen atom is, therefore, 2, or it is bivalent. The atom of calcium is also bivalent, for it is combined with two atoms of univalent chlorine. The nitrogen of *ammonia* has a valence of 3, or is *trivalent*; so is antimony in antimony chloride. Platinum and carbon have a valence of 4 — are *quadrivalent* — in platinum chloride and marsh gas, respectively. In phosphorus pentachloride (PCl_5) phosphorus is *quintivalent*. Sometimes the Greek numeral prefixes are used, as in *divalent*, *tétravalent*, and *péntavalent*.

The valence of elements is often represented by small *Roman* numerals placed a little *above* and to the *right* of the symbols. Thus Al^{III} means *trivalent* aluminum; Hg^{I} , *univalent* mercury; and Pt^{IV} , *quadrivalent* platinum.

134. Valence by Replacement. — The valence of an element is measured not only by the number of hydrogen atoms with which its atom has combined, but also by the number it has **replaced**. Thus sodium is *univalent* in sodium hydroxide (NaOH), because one atom of it has replaced **one** of the hydrogen atoms of water (HOH). In calcium hydroxide, $\text{Ca}(\text{OH})_2$, calcium is *bivalent*: its atom has replaced **two** hydrogen atoms (of 2 HOH). The formulas of the *sulphates* of these two elements (Na_2SO_4 and CaSO_4) also show their valences, for while it takes

only **one** *bivalent* calcium atom to replace the *two* hydrogen atoms in the molecule of sulphuric acid (H_2SO_4), it takes *two* atoms of univalent sodium.

135. Valences of Some Elements and Radicals.

	I.	II.	III.	IV.	V.	VI.
A. METALS.	Li. Na. K. Ag. Cu (ous). Hg (ous).	Fe (ous). Mn (ous). Sn (ous). Zn. Cu (ic). Hg (ic). Mg. Ca. Sr. Ba. Pb.	Fe (ic). Al. B. As. Sb. Bi.	Pt. Mn (in MnO_2). Sn (ic).		
B. NON-METALS.	H. F. Cl. Br. I.	O. S. (in sulphides).	N. P (ous).	C. Si. S (ous).	N (in N_2O_5). P (ic).	S (ic).
C. RADICALS.	NH_4 . <u>OH.</u> <u>ClO_3.</u> <u>NO_3.</u>	<u>SO_4.</u> <u>SO_3.</u> <u>CO_3.</u> <u>SiO_3.</u>	PO_4 .	SiO_4 .		

136. Formula Types Based on Valence.—Elements of equal valence unite atom for atom. Thus we have the formulas $\text{H}^{\text{I}}\text{Cl}^{\text{I}}$, $\text{C}^{\text{II}}\text{O}^{\text{II}}$, $\text{B}^{\text{III}}\text{N}^{\text{III}}$, and $\text{C}^{\text{IV}}\text{Si}^{\text{IV}}$. In representing molecules made up of two atoms of *unequal* valence, we use the rule that **valence** $\times$ *number of atoms*, in the case of the one

element, equals **valence** $\times$ *number of atoms*, in the case of the other.

Thus, an atom of a *bivalent* element unites with **two** atoms of a univalent element, as in $\text{H}_2\text{O}^{\text{I}}$ and $\text{Ca}^{\text{II}}\text{Cl}_2^{\text{I}}$. *Three* atoms of a *bivalent* element unite with *two* of a *trivalent* one, as in $\text{As}_2^{\text{III}}\text{S}_3^{\text{II}}$ and $\text{Mg}_3^{\text{II}}\text{N}_2^{\text{III}}$. A *quadrivalent* (tetravalent) atom unites with *four* univalent atoms, as in CH_4 and SiCl_4 , but with *two* bivalent atoms, as in CS_2 and SiO_2 .

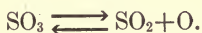
137. Valence of Radicals.

The idea of valence applies not only to the atoms of elements, but also to **radicals** (cf. § 105). Thus the radical **OH** has a valence of **I**, as in water (HOH) and in sodium hydroxide (NaOH). Nitric acid is HNO_3 , hence the *nitrate* radical, **NO₃**, is *univalent*. The radical **SO₄** is *bivalent*, as in sulphuric acid (H_2SO_4). Similarly, the radical **CO₃** of carbonic acid (H_2CO_3) is bivalent. Phosphoric acid is H_3PO_4 , hence **PO₄** is *trivalent*, while **SiO₄**, the *acid radical* of silicic acid (H_4SiO_4), is *quadrivalent*. If, therefore, we wish to write the formulas of the compounds formed by, let us say, **magnesium**, and these radicals, we apply the *valence rule* used for atoms, substituting "radicals" for "atoms" (cf. § 136). Hence magnesium *hydroxide* is $\text{Mg}(\text{OH})_2$; the *nitrate*, $\text{Mg}(\text{NO}_3)_2$; the *carbonate*, MgCO_3 ; the *sulphate*, MgSO_4 ; the *phosphate*, $\text{Mg}_3(\text{PO}_4)_2$; the *silicate*, Mg_2SiO_4 .

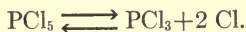
138. Multiple Valence.—The idea of valence applies only to **elements in combination**, and *not in the free state*. Thus, we cannot give the valence of iron unless we know the formula of some iron compound. If chlorine is univalent in the chlorides

(and it is), then iron is bivalent in *ferrous chloride* (FeCl_2), but trivalent in *ferric chloride* (FeCl_3). If oxygen is bivalent in the oxides, then carbon is bivalent in carbon monoxide (CO), and *quadrivalent* in the dioxide (CO_2). So phosphorus is trivalent in the formulas PCl_3 and P_2O_3 , but *quintivalent* (pentavalent) in PCl_5 and P_2O_5 . Sulphur is *bivalent* in hydrogen sulphide (H_2S) and all sulphides, *quadrivalent* in sulphur dioxide, and *sexivalent* (hexavalent) in sulphur trioxide. The element *argon* (*cf.* § 191), which forms no compounds, is of valence **zero** (0).

In general, the valence of an element is smaller at high temperatures than at low. Thus, sulphur trioxide breaks up when heated, —



Here the valence of sulphur falls from *six* to *four*. Phosphorus pentachloride, also, is dissociated when heated, —

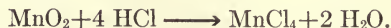


An element may show a higher valence when combined with some elements than with others. This is shown in the reaction by which chlorine is prepared (*cf.* § 115): —



In manganese dioxide the valence of manganese is probably 4 (*cf.* § 341). In a true double decom-

position, valences do not change; hence we should expect *manganese tetrachloride* to be formed: —



Instead, we obtain *manganous chloride*, MnCl_2 : the valence of the manganese falls from *four* to *two*.

139. Exercises.

1. If the valence of an element **M** is 1, write the formulas of its sulphate, carbonate, sulphide, nitrate, phosphate, and nitride. Write the formulas of the same compounds of an element, **R**, having a valence of 2.

2. Give the valence of each element in the following: Li_3N , Fe_2S_3 , ZnBr_2 , KI , SrO , As_2O_5 , SbCl_3 , PH_3 . Name each of these substances.

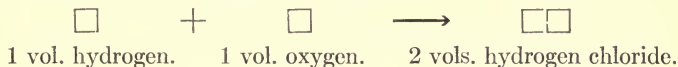
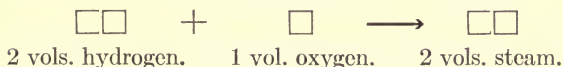
3. Considering *all but the first element* in each of the following to be a *radical*, give the valences of the first elements and of the radicals: KClO_3 , NaNO_3 , BaCO_3 , SrSO_4 , AlPO_4 , Ag_3PO_4 , $\text{Fe}(\text{OH})_3$, $\text{Bi}(\text{NO}_3)_3$. Name each of these compounds.

CHAPTER XII.

MOLECULAR WEIGHTS.

140. Combination by Volume; Gay-Lussac's Law.

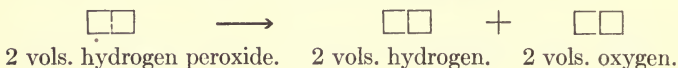
— We have already studied two cases of combination which show that elements unite, not only in definite proportions by *weight*, but also, if they are *gases*, in **definite proportions by volume**. The two cases are, (1) the union of hydrogen and oxygen to give steam (*cf.* § 63), and (2) the combination of hydrogen with chlorine to produce hydrogen chloride (*cf.* § 128). The proportions by volume in these cases are: —



The facts regarding combination by volume are summarized in Gay-Lussac's **Law of Definite Proportions by Volume**: *The volumes of reacting gases have a definite (and simple) relation to one another and to the volumes of the products, if these are gases.*

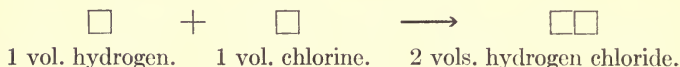
Just as elements may unite in more than one proportion by weight (*cf.* § 94), so *gaseous* elements may unite in more than one proportion by volume.

The case of hydrogen peroxide and water illustrates this: while two volumes of steam are formed from two volumes of hydrogen and **one** of oxygen, two volumes of gaseous hydrogen peroxide are composed of two volumes of hydrogen and **two** of oxygen.



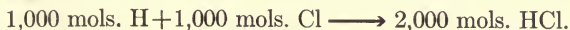
141. Avogadro's Hypothesis. — In §§ 98 and 99 we learned that molecules "occupy space." The **hypothesis of Avogadro** is that it takes *equal numbers of molecules to occupy equal spaces*, or, that *equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules*. Avogadro was an Italian physicist, and announced his hypothesis in 1811. Ampère reached the same conclusion in 1814.

142. The Molecules of Elements. — Avogadro's hypothesis gives us a basis for important deductions regarding the numbers of atoms in the molecules of gaseous elements. Let us take the case of *hydrogen chloride*.



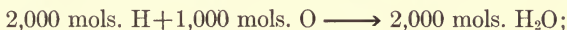
We have no idea how many molecules there actually are in any given volume, but let us assume that there are 1,000 molecules in one volume of hydrogen. Then one volume of chlorine will contain 1,000 molecules (Avogadro's hypothesis), and the **two** volumes of hydrogen chloride produced will contain **2,000**

molecules. But each molecule of hydrogen chloride must contain *some* hydrogen and *some* chlorine. It cannot contain a *whole* molecule of either, for there were only 1,000 molecules of each gas, —



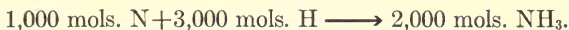
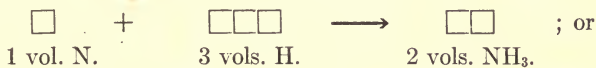
Hence, one molecule of hydrogen chloride must contain $\frac{1}{2}$ a molecule of hydrogen and $\frac{1}{2}$ a molecule of chlorine.

Similar reasoning leads to the conclusion that there must be a *half-molecule* of oxygen in the molecule of water (steam); for



therefore one molecule of steam must contain one molecule of hydrogen and $\frac{1}{2}$ a molecule of oxygen.

The facts regarding *nitrogen* are deduced from the equation for the union of nitrogen with hydrogen (*cf.* § 213), —



Hence, one molecule of ammonia must consist of $\frac{1}{2}$ a molecule of nitrogen and $1\frac{1}{2}$ molecules of hydrogen.

The half-molecules of these four elementary gases are assumed to be the atoms, hence we conclude that the molecules of hydrogen, nitrogen, oxygen, and chlorine consist of two atoms each.

143. Molecular Weights of Gases. — Avogadro's hypothesis is also the basis of **molecular weights**. We cannot get at the *actual* weights of molecules, but we can get at their **relative** weights, *if we assume that there are equal numbers of molecules in equal*

volumes. Thus, since the *liter* of oxygen is practically 16 times as heavy as the *liter* of hydrogen ($1\frac{1}{8}\frac{2}{9}$), the cubic centimeter, and cubic millimeter, of oxygen must be 16 times as heavy as the cubic centimeter, and cubic millimeter, respectively, of hydrogen. We conclude, then, that the **molecule** — the *smallest* volume — of oxygen is 16 times as heavy as the **molecule** of hydrogen. What is true of *these* two gases is true of others: *the ratio of the weights of equal volumes of two gases equals the ratio of their molecular weights*. If we assume the molecular weight of some one gas as a **standard**, we can find the molecular weights of the others in terms of this standard. The atomic weight of oxygen is taken as exactly 16 (*cf.* § 97); there are two atoms in the oxygen molecule (*cf.* § 142); hence, the molecular weight of oxygen is taken as *exactly* 32. *This is the standard of molecular weights.*

The molecular weight of a gas is thus determined from the equation, —

$$\frac{\text{Wt. of given vol. of gas}}{\text{Wt. of same vol. of oxygen}} = \frac{\text{Mol. wt. of gas}}{\text{Mol. wt. of oxygen}}.$$

By substituting known values in this equation we can calculate the molecular weight of hydrogen (x) thus: —

$$\frac{.09}{1.429} = \frac{x}{32}; \text{ whence } x = 2.016.$$

144. Vapor Density Methods.

The hypothesis of Avogadro applies not only to gases, but also to liquids and solids that can be vaporized. Thus, a liter of *steam*, or of gaseous *acetic acid* (cf. § 535) is assumed to contain practically as many molecules as a liter of oxygen *under the same conditions*. To get the molecular weights of such substances, we use the equation of § 143. To distinguish the methods used for *vapors* from those used for gases, the former are called "vapor density" methods.

Victor Meyer's Method. Suppose we wish to get the approximate molecular weight of *chloroform*, boiling at 61°C . In the method of Victor Meyer (Fig. 35), a weighed amount of the chloroform is dropped into the tube *A* and vaporized; the air which is expelled through the delivery tube and collected in the graduated tube is a measure of the volume of the chloroform vapor. We thus obtain the weight of a given number of cubic centimeters of chloroform vapor. By comparing this weight with the weight of an equal volume of oxygen, we can get the molecular weight of chloroform.

The tube *A* is raised to any required temperature by boiling some liquid in the jacket *B*; in the case of chloroform, water might be used.

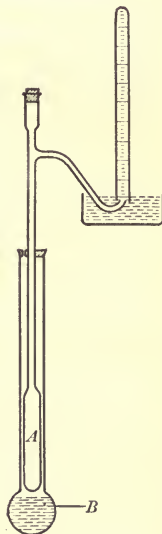


FIG. 35.

145. Gram-Molecular Weight and Volume. —

We call 32 grams of oxygen, *i. e.*, as many grams of it as there are units in its molecular weight, a **gram-molecular weight** of oxygen (cf. § 103). For carbon

dioxide (CO_2) the gram-molecular weight is 44 grams. The term "gram-molecular weight" is often abbreviated to *molar weight*, or *mole*.

Now, if we determine the volume, under standard conditions, of a gram-molecular weight of oxygen, we find it to be **22.4 liters** ($32 \div 1.429 = 22.4$). The volume of a gram-molecular weight of a gas is called the **gram-molecular volume**, and trial shows that the gram-molecular volumes of all gases are the same, *viz.*, **22.4 liters**. The gram-molecular (or *molar*) volume is equivalent to the volume of a cube 28.19 cm. (about 11.1 inches) on each edge.

The gram-molecular volume is the basis of a second method of getting the molecular weights of gases: *we simply determine the weight, under standard conditions, of 22.4 liters of the gas*. This gives us the gram-molecular weight.

The method does not differ in principle from that of § 143. This is shown by the following equations: —

$$\frac{\text{Wt. of 1 l. of gas}}{\text{Wt. of 1 l. of oxygen}} = \frac{\text{Mol. wt. of gas}}{\text{Mol. wt. of oxygen}}.$$

Then, $\text{wt. of 1 l. gas} \times \text{mol. wt. of O} = \text{wt. of 1 l. O} \times \text{mol. wt. of gas}$.

Substituting known values for oxygen we have, —

$$\text{Wt. of 1 l. gas} \times 32 = 1.429 \times \text{mol. wt. of gas};$$

$$\text{Wt. of 1 l. gas} \times 1.429 = \text{mol. wt. of gas};$$

$$\text{Wt. of 1 l. gas} \times 22.4 = \text{mol. wt. of gas}.$$

146. Molecular Weights of Soluble Substances. —

The foregoing methods of determining molecular weights do not apply to substances that cannot be vaporized. For *soluble* substances, however, methods are available that are based upon the properties of solutions, *viz.*, upon the *freezing point*, the *boiling point*, and the *osmotic pressure* (*cf.* § 149). These methods all depend upon the fact that solids and liquids in solution have many of the properties they would possess if they were *gaseous*. Solution methods do not apply to *acids*, *bases*, and *salts* (*cf.* § 173).

147. Freezing Point Method. —When sugar is dissolved in water it retards the water molecules in their change to the solid state, hence the solution freezes at a lower temperature than pure water. Other solutes have a similar effect. Now, we can get the molecular weights of such substances as *alcohol* (C_2H_6O) and *glycerine* ($C_3H_8O_3$) by “vapor density” methods (*cf.* § 144). The gram-molecular weight of alcohol is 46 g., and that of glycerine 92 g. If 46 g. of alcohol and 92 g. of glycerine are each dissolved in 1,000 grams of water, the solutions freeze *at the same temperature*, *viz.*, $-1.89^\circ C$. We ought to expect this, since *the solutions contain equal numbers of molecules* of the solute. If we add cane-sugar to 1,000 grams of water until the freezing-point of the solution is $-1.89^\circ C$., we can get the gram-molecular weight of cane-sugar. It will take

about 342 grams, hence the molecular weight of cane-sugar is about 342. In the case of *urea* (CON_2H_4), 60 grams would be required; of *grape-sugar*, 180 grams; hence the molecular weights of these substances are 60 and 180, respectively.

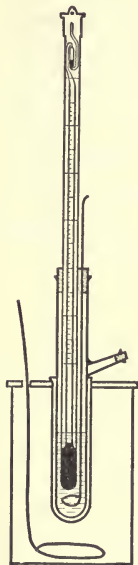


FIG. 36.

In practice, much smaller amounts of solute and solvent are used, but the principle is as stated. The apparatus for molecular weight determinations by the freezing-point method is shown in Fig. 36. It consists essentially of a delicate thermometer, reading to $\frac{1}{1000}$ th of a degree, and a thin glass tube to hold the solvent. The jar surrounding the tube contains a suitable freezing mixture. This is stirred by the wire stirrer. First, the freezing-point of the pure solvent is obtained, then a weighed amount of solute is added through the side-tube, and the freezing-point of the solution is determined. The difference is the *freezing-point depression*. The formula for the calculation of the molecular weight is, —

$$\left. \begin{array}{l} \text{Depression,} \\ \text{in aqueous} \\ \text{solution,} \end{array} \right\} = \frac{1.89 \times \text{wt. of solute} \times 1,000}{\text{Mol. wt. of solute} \times \text{wt. of solvent}}$$

1.89 is the gram-molecular depression for water; for other solvents it must be determined by means of a solute of known molecular weight.

148. Boiling Point Method.

Just as a solute retards the freezing of the solvent, so it retards its boiling, *i. e.*, it raises the boiling temperature. Of course the

solute must not be volatile at the boiling temperature of the solvent. But, just as gram-molecular weights of cane-sugar, grape-sugar, urea, etc., each dissolved in 1,000 grams of water, give solutions having the same freezing-point, so they give solutions of *the same boiling temperature*. While water boils at 100°C ., under 760 mm., a solution containing a gram-molecular weight of solute in 1,000 grams of water boils at 100.52°C . Hence, by adding a solute of unknown molecular weight to 1,000 grams of water at 760 mm., until the boiling-point of the solution reaches 100.52°C ., we can determine its gram-molecular weight.

149. Osmotic Pressure.

Under "hydrogen," § 52, we learned that if a porous cup of air (Fig. 14) is immersed in hydrogen, this gas enters the cup so much more rapidly than air can get out, that there is an increase of pressure *inside* the cup. Suppose the "cup" were a closed vessel made of *palladium*, a metal which "occludes" hydrogen (cf. § 53), and through which hydrogen can pass while air cannot (Fig. 37). Assume that the air inside was under one atmosphere pressure. Hydrogen would enter until its pressure *inside* was equal to that outside, viz., *one atmosphere*. But, since the air originally in the palladium vessel had a pressure of one atmosphere, the total pressure inside would now be **two atmospheres**. If the vessel communicated with a column of mercury, the height to which the mercury was raised would indicate the excess of pressure *inside* the palladium vessel.

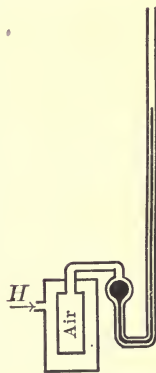


FIG. 37.

If we replace the palladium vessel of air by a *water solution of sugar*, and the surrounding hydrogen by *pure water*, we shall

have the corresponding phenomenon for solutions. We call it **osmosis**. The sugar solution may be in a thistle tube (Fig. 38), the "thistle" of which is covered water-tight with parchment



FIG. 38.

paper. An egg-shell, with a tube attached, may be used instead; here the lining membrane of the shell replaces the parchment. The parchment and membrane are **semi-permeable**, *i. e.*, they permit the water molecules to pass freely, but **not** the sugar molecules (or only a very little). Water enters the "cell" to make the pressure of water *inside* equal that without. The result is to increase the volume of liquid inside, and to force some of it up the tube. If the membrane is strong enough, and permits no sugar to pass outward, the column will rise until its hydrostatic pressure causes water to leave the cell as rapidly as it enters. When this condition of *equilibrium* is reached, the excess of inside pressure is the **osmotic pressure** of the solution. For accurate work osmotic pressure cells

are made of strong earthenware into the pores of which *cupric ferrocyanide*, $\text{Cu}_2\text{Fe}(\text{CN})_6$, has been precipitated.

Now, if *gram-molecular weights of cane-sugar, grape-sugar, urea, etc.*, are dissolved in 1,000 grams of water, the osmotic pressures of the solutions, like the boiling-point elevations and freezing-point depressions, are equal. Osmotic pressure methods are not used much in getting molecular weights because the other methods are easier to carry out. Just as gas pressure is proportional to the density (*cf.* § 40), so the osmotic pressure is proportional to the *concentration* of the solution. Osmotic pressure is also proportional to the absolute temperature (Charles' Law).

150. Methods of Obtaining Exact Molecular Weights.

All the methods described give only *approximate* molecular weights; *exact* molecular weights are found by quantitative analysis.

The methods used may be illustrated by the case of *acetic acid*, $\text{HC}_2\text{H}_3\text{O}_2$; the exact molecular weight of this substance may be found by a study of its *silver* salt, $\text{AgC}_2\text{H}_3\text{O}_2$.

Silver acetate contains silver, carbon, hydrogen, and oxygen. The per cent of the silver being found by analysis to be 64.65, that of the remainder of the molecule must be 35.35. The atomic weight of silver, if we take the atomic weight of oxygen as *exactly* 16, is very nearly 107.94; the weight (x) of all of the silver acetate molecule *except* the silver is, therefore, found from the equation, —

$$x = 107.94 \times \frac{35.35}{64.65}.$$

Hence $x = 59.02$.

Since acetic acid is silver acetate with the silver replaced by hydrogen, we must add to 59.02 the number representing the weight of the hydrogen that 107.94 parts of silver replace. This is 1.008. Hence the exact molecular weight of acetic acid is 60.028.

151. Exercises.

1. If 1 volume of phosphorus vapor unites with 6 volumes of chlorine to give 4 volumes of phosphorus trichloride, how many atoms, at least, are there in a molecule of phosphorus?

2. If, at the boiling point of sulphur, 1 c.c. of the vapor unites with 8 c.c. of oxygen to give 8 c.c. of sulphur dioxide, calculate the number of sulphur atoms in a molecule.

3. If 275 c.c. of a gas at 25°C . and 715 mm. weigh 0.46 gram, calculate the molecular weight of the gas.

4. The molecular weight of a gas is 60. Calculate the weight of 290 c.c. of it at 13°C . and 800 mm.

5. A 500 c.c. flask of air weighed 40.495 grams at 18°C . and 740 mm. When filled with ether vapor at 50°C . and 740 mm.

it weighed 41.2605 grams. Calculate the weight of one liter of ether vapor at 50° C. and 740 mm. Calculate the molecular weight of ether.

6. In a Victor Meyer vapor density apparatus 0.1387 gram of a compound expelled 47.2 c.c. of dry air at 24° C. and 735 mm. What is the molecular weight of the compound?

CHAPTER XIII.

ATOMIC WEIGHTS.

152. Determination of Atomic Weights. — As was stated in § 97, we were obliged to postpone the determination of atomic weights until we had learned how the molecular weights are obtained. Now, since the common methods of getting molecular weights, described in §§ 143 to 145, apply only to gases, the atomic weights of elements are determined *primarily* from the molecular weights of the gaseous compounds of the elements. The tables will show how the method works for chlorine and carbon.

I.	II.	III.	IV.
COMPOUNDS OF CHLORINE.	GRAM- MOLECULAR WEIGHT OF COMPOUND.	PER CENT OF CHLORINE IN COMPOUND.	GRAMS OF CHLORINE IN THE GRAM-MO- LECULAR WEIGHT OF COMPOUND.
Hydrogen chloride.	36.5	97.26	35.5
Acetyl chloride.	78.5	45.22	35.5
Ethyl chloride.	64.5	55.03	35.5
Carbonyl chloride.	99.	71.71	71.
Chromium oxychloride.	155.1	45.8	71.
Chlorine gas.	71.	100.	71.
Arsenic trichloride.	181.5	58.67	106.5
Phosphorus trichloride.	137.5	77.45	106.5
Carbon tetrachloride.	154.	92.21	142.
Silicon tetrachloride.	170.4	83.33	142.
Tantalum chloride.	360.5	49.24	177.5
Hexachlorethane.	237.	89.87	213.

The chlorine compounds of column I can all be vaporized and their molecular weights determined by vapor density methods (*cf.* § 144). *For convenience*, the molecular weights have been made *exact*. In actual determinations the figures would be only approximate. The per cent of chlorine (column III) in each compound is found, **with great accuracy**, by *quantitative chemical analysis*. Multiplying the numbers of column II by those of III, *taken as hundredths*, gives the figures of column IV. These represent the weight of the *atoms* of chlorine in the *molecule* of the compound, or the **grams** of chlorine in the *gram-molecular weight* of the compound. The smallest numbers in this column are approximately 35.5, and the larger ones almost exact multiples of 35.5. The atomic weight of chlorine is, thus, *approximately 35.5*.

In the case of **carbon** (see table) we can make an *additional* column (II) since the compounds named

I.	II.	III.	IV.	V.
COMPOUNDS OF CARBON.	WEIGHT, IN GRAMS, OF ONE LITER.	GRAM-MO- LECULAR WEIGHT.	PER CENT OF CARBON IN COMPOUND.	GRAMS OF CARBON IN GRAM-MOLEC- ULAR WEIGHT OF COMPOUND.
Carbon monoxide.	1.251	28.02	42.86	12.01
Carbon dioxide.	1.977	44.28	27.27	12.08
Marsh gas.	0.717	16.06	75.	12.08
Ethylene.	1.25	28.00	85.71	23.99
Acetylene	1.16	25.98	92.31	23.98
Propane.	1.97	44.13	81.82	36.11

are all gaseous under ordinary conditions. The atomic weight is, apparently, about 12.

Definition of Atomic Weight. — We are now ready to define atomic weight. The atomic weight of an element is the number representing the **smallest weight of the element in the gram-molecular weight of any of its gaseous compounds.**

153. Accuracy of the Method. — The correctness of the atomic weights of chlorine and of carbon, as found from the tables of § 152, depends upon the accuracy of the molecular weights. Since these cannot be determined with great exactness by the methods used; the atomic weights derived from them are only *approximate*. **Exact atomic weights are obtained from the equivalent weights** (*cf.* § 97). The equivalent weight of chlorine is 35.45. Since the approximate atomic weight and the equivalent weight are almost equal numerically, *the accurate equivalent* is taken as the atomic weight.

In the case of *carbon* the equivalent weight, as obtained from the ratio of carbon to oxygen in carbon dioxide, is very nearly 3.003. As the atomic weight obtained from the table of § 152 is about 12, the *exact* atomic weight is obtained by multiplying the equivalent weight by 4. This makes the atomic weight of carbon 12.01. The factor by which we multiply the equivalent weight to get the atomic weight is the **valence** (*cf.* § 132).

Note that the atomic weight found from the molecular weights is the *greatest* atomic weight the element can have. The study of new compounds of the element may make it necessary for chemists to choose some smaller number, but not a larger one.

154. Summary of the Method.

The general method of selecting the atomic weights of such elements as hydrogen, nitrogen, bromine, iodine, sulphur, phosphorus, arsenic, and some others is as given for chlorine and carbon. In each case we must have the following data: —

(1) The molecular weights of several gaseous compounds of the element.

(2) The number of grams in the gram-molecular weight of each compound that represents the weight of the element itself. The smallest of these is the approximate atomic weight.

(3) The equivalent weight of the element. This is either numerically equal to the atomic weight, or must be multiplied by some small integer to give it.

155. Dulong and Petit's Rule. — Substances differ greatly in their *capacity for heat*, that is, in the **amount** of heat acquired (or lost) by them when they are heated (or cooled) through a given range of temperature. This varying heat capacity, or **specific heat**, of different substances is measured by the number of units of heat (*calories*, cf. § 55) a given weight of the substances can impart to a given weight of another substance, such as water. If we heat two 100 g. balls, one of *iron* and one of *lead*, to the same temperature, say 200° C., and plunge them into equal weights of water at 20° C., the water will

be heated to a higher temperature by the iron ball than by the one of lead. The *specific heat* of iron is greater than that of lead. Water has a greater heat capacity than any other substance except hydrogen (*cf.* § 71).

In 1819, Dulong and Petit observed the existence of the rule which is called by their names; the rule may be stated as follows: —

The specific heat of a solid element multiplied by its atomic weight is a constant (about 6.25). Some illustrations appear in the following table: —

ELEMENT.	SPECIFIC HEAT.		ATOMIC WEIGHT.		ATOMIC HEAT.
Sodium.	0.29	×	23	=	6.7
Potassium.	0.166	×	39	=	6.5
Iron.	0.112	×	56	=	6.3
Silver.	0.057	×	108	=	6.1
Tin.	0.054	×	118	=	6.4
Gold.	0.032	×	196	=	6.3
Mercury (solid).	0.032	×	200	=	6.4
Lead.	0.031	×	206.4	=	6.4

The table shows that the higher the atomic weight is, the lower is the specific heat. The complete list of specific heats is given in Appendix iii.

It is apparent that the rule of Dulong and Petit may be used to determine the *approximate* atomic weight of an element. Thus, knowing the specific heat of *cadmium* to be 0.0567, we can at once get

its approximate atomic weight. We simply solve for x in the equation,

$$\frac{6.25}{0.0567} = x.$$

Hence $x = 110$.

The exact atomic weight of cadmium is about 112.

156. Application of Atomic Weight Methods.

The methods used in actually getting the atomic weight of an element may be illustrated by the case of *zinc*. The method used for chlorine will not apply here; we must, therefore, study the action of zinc with elements of *known* atomic weight, *e. g.*, with hydrogen, chlorine, and oxygen.

When zinc is dissolved in certain dilute acids, it sets free hydrogen; we can thus get the **equivalent** of the zinc. Now, if for each atom of zinc dissolved an atom of hydrogen is set free, the gram-atomic weight of zinc must equal its equivalent weight, *i. e.*, 32.7 grams.

A second element with which we can compare zinc is **chlorine**. The compound of these two elements, zinc chloride, may be made either (1) by dissolving zinc in hydrochloric acid and evaporating the solution, or (2) by burning zinc in chlorine.

The relation of zinc to chlorine in zinc chloride, as determined by quantitative analysis, is about as 32.7 : 35.5. Hence, if chlorine and zinc have united atom for atom, and the atomic weight of chlorine is 35.5, the atomic weight of zinc must be 32.7.

Let us, however, consider a *third* compound of zinc, *viz.*, its *oxide*. This substance may be made by heating zinc in oxygen, or, better, by dissolving zinc in dilute nitric acid and heating the zinc nitrate formed to a high temperature. The proportions of the elements in zinc oxide are, — zinc, 65.4 parts, to oxygen, 16 parts. Here, also, we might assume that zinc and the other

element are united atom for atom; if so, the atomic weight of zinc is 65.4.

To compare these results let us write them down together:—

(1) One gram-atomic weight of hydrogen (1 gram) was replaced by 32.7 grams of zinc.

(2) One gram-atomic weight of chlorine (35.5 grams) united with 32.7 grams of zinc.

(3) One gram-atomic weight of oxygen (16 grams) united with 65.4 grams of zinc.

Evidently we cannot assume that one atom of zinc unites with one atom of the other element in each of the three cases; for we cannot have some zinc atoms with a weight of 32.7 each, and others with a weight twice as great. If the atomic weight of zinc is 32.7, *one* atom of oxygen must unite with *two* atoms of zinc to form zinc oxide; if, however, the atomic weight of zinc is 65.4, *two* atoms of hydrogen must have been replaced by *one* of zinc, and *two* atoms of chlorine must have united with *one* of zinc.

The *molecular weight* of zinc chloride, or of zinc oxide, would help us; that of zinc chloride is the one used; for the weight of a known volume of its vapor has been obtained. By a solution of the equation, —

$$\frac{\text{Wt. of 1 l. zinc chloride vapor}}{\text{Wt. of 1 l. oxygen}} = \frac{\text{Mol. wt. of zinc chloride}}{\text{Mol. wt. of oxygen}},$$

the molecular weight of zinc chloride was found in an actual experiment to be about 134. This result is sufficiently accurate to enable us to decide that the molecular weight of zinc chloride is 136.4 rather than *one-half* or *twice* this number.

A molecule of zinc chloride thus contains 65.4 parts of zinc and 71 parts (two atoms) of chlorine. We do not, however, know whether the two atoms of chlorine are united with *one* atom of zinc having a weight of 65.4, or with *two*, each having a weight of 32.7; or with *three*, each having a weight of 21.8, etc.

We now apply Dulong and Petit's rule. By substituting the specific heat of zinc, found by experiment (0.094), in the expression,

$$\frac{6.25}{\text{specific heat}} = \text{atomic weight},$$

we obtain 66.5 for the *approximate* atomic weight of zinc. This shows us that the number 65.4 is to be taken rather than any sub-multiple of it.

157. Exercises.

1. Use the following data to calculate the approximate atomic weight of nitrogen. If the equivalent weight is 4.67, what is the exact atomic weight?

WEIGHT OF 1 LITER, IN GRAMS.		PER CENT OF NITROGEN.
Nitrogen,	1.256	100.
Nitric oxide,	1.34	46.67
Nitrous oxide,	1.97	63.64
Ammonia,	0.762	82.35

2. From the following data calculate the atomic weight of hydrogen. How is the exact atomic weight obtained?

WEIGHT OF 1 LITER, IN GRAMS.		PER CENT OF HYDROGEN.
Hydrogen chloride,	1.61	2.74
Hydrogen bromide,	3.61	1.23
Hydrogen,	0.09	100.00
Hydrogen sulphide,	1.542	5.88
Ammonia,	0.762	17.65
Marsh gas,	0.717	25.00

3. What is the atomic weight (approximate) of an element if its specific heat is 0.033? If it is 0.0952?
4. The specific heat of arsenic is 0.0814, and its vapor is 9.37 times as heavy as oxygen. How many atoms are there in its molecule?
5. Calculate the specific heats of the following elements from Dulong and Petit's Rule: gold, nickel, potassium, lead, zinc.

CHAPTER XIV.

ACIDS, BASES, AND SALTS.

158. Acids. — In all of our study of Chemistry we shall have to deal constantly with bodies belonging to the classes *acids*, *bases*, or *salts*. Let us first consider some of the acids. One of these, viz., *hydrochloric acid*, we have already studied at some length; other important acids are *nitric acid*, *sulphuric acid*, *acetic acid*, and *tartaric acid*. Only a short description of these will be given here.

Nitric acid, HNO_3 , is a colorless liquid. It ordinarily has a sharp odor and is very corrosive in concentrated form. It turns the skin yellow. A dilute solution of nitric acid is sour, turns blue litmus and neutral litmus pink, decomposes carbonates, *e. g.*, marble, or calcium carbonate, and acts upon many metals.

Sulphuric acid, H_2SO_4 , is a heavy, oily liquid which dissolves in water with the evolution of much heat. It chars organic substances, and, therefore, becomes dark colored when exposed for a time to the dust of the air. Its dilute solution has a sour taste, and acts upon litmus and carbonates as nitric and hydrochloric acids do. With many metals dilute sulphuric acid gives sulphates and hydrogen.

Acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, is a colorless, sharp-smelling liquid. Like the other acids, it has a sour taste, acts upon litmus, and decomposes carbonates. Vinegar is a dilute solution of acetic acid.

Tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, is a white, crystalline solid, soluble in water. Its solution has properties similar to those of the other acids.

All of the acids named, except hydrochloric acid, may be looked upon as water joined to an oxide. The oxide is called the **anhydride** of the acid.

Thus nitrogen pentoxide, N_2O_5 , is the *anhydride* of nitric acid, for



Similarly, sulphur trioxide, SO_3 , is the anhydride of sulphuric acid.

The most important property of all acids is their power of reacting with the hydroxides of metals. When a solution of any of the above acids is treated with a solution of a metal hydroxide, *e. g.*, sodium hydroxide, an evolution of heat takes place, and if the correct amount of sodium hydroxide is used, the *taste* of the acid, its *power to change litmus*, and to act upon *carbonates* and *metals*, will all disappear. The acid has been **neutralized** by the sodium hydroxide.

159. Bases. — The general properties of sodium hydroxide and its relation to water have already been given (*cf.* § 74).

Sodium hydroxide, NaOH , is a white solid which attracts moisture and carbon dioxide from the air, and thus becomes converted into sodium carbonate. Its solution changes *pink* and neutral litmus to *blue*, feels *soapy* to the touch, and has a *bitter, alkaline* taste.

Potassium hydroxide, KOH , resembles sodium hydroxide

closely. Its aqueous solution has properties *almost* identical with those of sodium hydroxide.

Ammonium hydroxide, NH_4OH , is not known in the free condition. Its aqueous solution smells strongly of *ammonia*, owing to the constant evolution of this gas, but its reaction to litmus, etc., is much like that of sodium and potassium hydroxides.

Calcium hydroxide, $\text{Ca}(\text{OH})_2$, is a white solid made by adding the necessary amount of water to *quicklime*, CaO . Calcium hydroxide is slightly soluble in water; the solution is called *lime-water*.

Barium hydroxide, $\text{Ba}(\text{OH})_2$, is much more soluble than calcium hydroxide. Its solution is called *baryta water*.

All of these hydroxides, and many more, are grouped together under the general name, *bases*. The most *active* bases are sodium and potassium hydroxides, which, with ammonium hydroxide, are called **alkalies**.

As has already been stated (*cf.* § 75), hydroxides may be looked upon as water with half of its hydrogen replaced by a metallic element. This is true of calcium hydroxide, having the formula

$\text{Ca} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$, no less than of sodium hydroxide, NaOH .

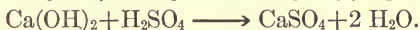
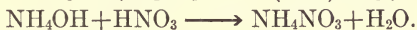
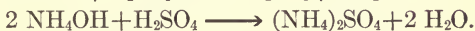
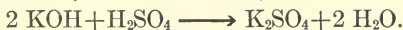
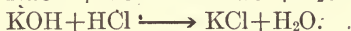
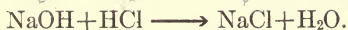
The formula $\text{Ca} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$, however, must be thought of as derived

from $2 \text{H}_2\text{O}$, or $\left\{ \begin{smallmatrix} \text{H}-\text{OH} \\ \text{H}-\text{OH} \end{smallmatrix} \right.$. Similarly, the formula $\text{Fe} \begin{smallmatrix} \text{OH} \\ \text{OH} \\ \text{OH} \end{smallmatrix}$ or

$\text{Fe}(\text{OH})_3$, for ferric hydroxide, is derived from $\left\{ \begin{smallmatrix} \text{HOH} \\ \text{HOH} \\ \text{HOH} \end{smallmatrix} \right.$ by re-

placing half of the hydrogen there represented by Fe.

160. Neutralization.—A comparison of the formulas of the hydroxides named will show that *they all contain the group OH* (called **hydroxyl**) taken one or more times. On the other hand, the formulas of the acids show that *the acids all contain hydrogen*, taken *once, twice*, etc., in each formula. Furthermore, the neutralization of acids by bases produces *salts* and *water*, as is shown by the following equations:—



The *neutralization of properties* which takes place when a basic hydroxide and an acid are brought together thus *consists in the union of the hydrogen of the acid with the hydroxyl of the base to form water*. The *metal* of the hydroxide and *all but the hydrogen* of the acid are found, on evaporation of the water, combined in the resulting *salt*.

The formula of an acid *minus* the replaceable hydrogen is called the **acid radical** (*cf.* § 105).

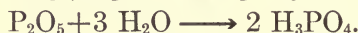
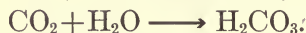
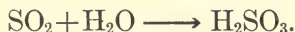
161. Two Classes of Oxides.—We have already learned (*cf.* §§ 8 and 72) that metals and non-metals differ decidedly both in physical and in chemical properties. Both unite with oxygen, giving **oxides**,

but the two classes of oxides give rise to two *fundamentally different* classes of substances, *bases* and *acids*.

The **oxides of metals**, such as CaO and Na_2O , unite with water to produce **bases**:



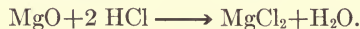
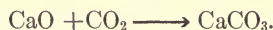
The **oxides of non-metals**, on the other hand, give **acids** when they unite with water: —



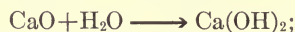
The oxides of non-metals are thus the **anhydrides** of *oxygen acids* (*cf.* § 168); the oxides of metals are the anhydrides of *basic hydroxides*.

162. Action of Oxides with Acids and Bases.

Oxides of metals react with **acid anhydrides** to give **salts**, or with *acids* to give *salts and water*.



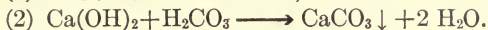
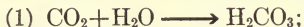
If water is present, the equations ought to show, (1) the union of oxide and water, and (2) the action of hydroxide and acid: —



Also,



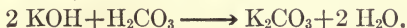
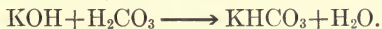
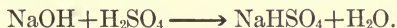
When the gas *carbon dioxide* acts upon lime-water, we write: —



✓ **163. Salts.** — Salts may be looked upon as *acids* in which hydrogen has been replaced by **metals**. By no means *all* of the hydrogen of many acids is replaceable by metals, but when all that can be has been replaced, the resulting substance is called a *normal salt*. The normal salts formed by such strong acids as sulphuric acid, nitric acid, and hydrochloric acid with such electro-positive metals as sodium, potassium, and the group ammonium, are *neutral* in their properties, *i. e.*, they will not turn blue litmus red, nor red, blue, but will produce in *sensitive* litmus a characteristic lavender color. The taste of such salts resembles that of common salt.

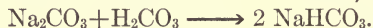
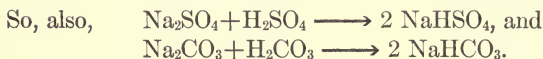
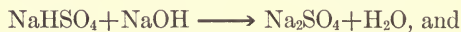
But a salt may be *normal* without being *neutral*. Thus, sodium carbonate is a normal salt, but the reaction of its solution toward litmus is that of a base. Ferric sulphate solution, on the contrary, has an acid reaction.

164. Acid Salts. — In many cases, the hydrogen of the acid is replaceable by metals in *two* or more stages (*cf.* § 126); hence, *there may be two or more salts formed by the acid with the same basic hydroxide*. The following equations illustrate this: —



The substance NaHSO_4 is *sodium hydrogen sulphate*, while Na_2SO_4 is *sodium sulphate*. Similarly, KHCO_3 is *potassium hydrogen carbonate*, but K_2CO_3 is *potassium carbonate*.

The salts in which there is still replaceable hydrogen are called *acid salts*. Acid salts may usually be converted into normal salts by the addition of enough of the hydroxide to replace all the replaceable hydrogen, and, conversely, normal salts may be converted into acid salts by treatment with free acid. Thus: —



Solutions of acid salts have *usually* an acid reaction toward litmus, but not always; for the reaction may sometimes be *alkaline*, as in the case of sodium hydrogen carbonate and disodium hydrogen phosphate, Na_2HPO_4 .

165. Basic Salts. — A salt may be considered from two points of view, either (1) as an *acid*, the hydrogen of which has been replaced by a metal, or (2) as a *hydroxide* with its hydroxyl (OH) replaced by a non-metallic element or by an acid radical (*cf.* § 160). Thus sodium chloride, NaCl , may be looked upon as hydrochloric acid, HCl , with hydrogen replaced by sodium, or as sodium hydroxide, NaOH , with hydroxyl replaced by chlorine. Similarly, calcium

chloride, CaCl_2 , is calcium hydroxide, $\text{Ca}(\text{OH})_2$, with hydroxyl replaced by chlorine; and calcium sulphate, CaSO_4 , is calcium hydroxide with hydroxyl replaced by the acid radical SO_4 . Now, just as in sulphuric acid, H_2SO_4 , the hydrogen may be replaced half at a time, so in calcium hydroxide the hydroxyl groups may be substituted, *theoretically*, in *two* stages. We *might*, therefore, have from calcium hydroxide and hydrochloric acid two compounds,

(1) $\text{Ca} \begin{smallmatrix} \text{OH} \\ \text{Cl} \end{smallmatrix}$, and (2) $\text{Ca} \begin{smallmatrix} \text{Cl} \\ \text{Cl} \end{smallmatrix}$. Just as we call a salt

which still contains replaceable hydrogen an *acid* salt, so we call one having replaceable hydroxyl groups a *basic salt*.

To illustrate: Just as *phosphoric acid*, H_3PO_4 , may have *two acid sodium salts*, viz., NaH_2PO_4 and Na_2HPO_4 , so *bismuth hydroxide*, $\text{Bi}(\text{OH})_3$, might have *two basic nitrates*, viz., $\text{Bi} \begin{smallmatrix} (\text{OH})_2 \\ \text{NO}_3 \end{smallmatrix}$ and $\text{Bi} \begin{smallmatrix} \text{OH} \\ (\text{NO}_3)_2 \end{smallmatrix}$.

The normal nitrate is, of course, $\text{Bi}(\text{NO}_3)_3$.

It is to be noted, however, that some basic salts have, apparently, a more complex constitution.

166. Basicity and Acidity. — The number of stages in which the replaceable hydrogen of an acid can be substituted by metals determines the **basicity** of the acid. Thus, hydrochloric acid, HCl , nitric acid, HNO_3 , and acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, are *monobasic*

acids; carbonic acid, H_2CO_3 , and sulphuric acid, H_2SO_4 , are *dibasic*; while phosphoric acid, H_3PO_4 , is *tribasic*.

In the same way, the number of stages in which the hydroxyl groups of a basic hydroxide might be replaced by acid radicals or by non-metals determines, roughly, the *acidity* of the hydroxide. Thus sodium hydroxide and potassium hydroxide are *monacidic* bases; calcium hydroxide, $\text{Ca}(\text{OH})_2$, and barium hydroxide, $\text{Ba}(\text{OH})_2$, are *diacidic*; while bismuth hydroxide, $\text{Bi}(\text{OH})_3$, is *triacidic*.

167. Equivalent Solutions of Acids, Bases, and Salts.

Solutions are often made of such a "strength," or concentration, that they contain one gram-molecular weight of solute in each liter of solution. Such solutions are called gram-molecular, or *molar*, solutions. Thus, 36.5 grams of hydrogen chloride (HCl), 98 grams of sulphuric acid (H_2SO_4), 58.5 grams of common salt (NaCl), or 40 grams of sodium hydroxide (NaOH), each in a **liter** of their solutions, form **molar** solutions; 1 c.c. of a molar solution of NaOH will just neutralize 1 c.c. of a molar solution of HCl , and will form 0.001 of a molar weight of NaCl , *i. e.*, .0585 gram. But it will take **2 c.c.** of molar NaOH solution to neutralize 1 c.c. of molar H_2SO_4 . Obviously, it will also take **2 c.c.** of molar HCl to neutralize 1 c.c. of molar *barium hydroxide*, $\text{Ba}(\text{OH})_2$. In order to have solutions of such concentration that they will react, cubic centimeter for cubic centimeter, chemists use **normal** solutions. A normal solution of an *acid* contains

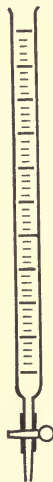


FIG 39.

1 gram of replaceable hydrogen (an **equivalent weight**) per liter; normal solutions of *bases* and *salts* contain an **equivalent weight of metal** per liter. Thus, normal solutions of NaOH ,

HCl, and NaCl have the same concentrations as molar solutions of these substances; but a normal solution of H_2SO_4 contains 49 grams ($98 \div 2$) of solute per liter, and one of $\text{Ba}(\text{OH})_2$, 85.5 g. of solute per liter. Decinormal $\left(0.1 \text{ N, or } \frac{\text{N}}{10}\right)$, half-normal $\left(\frac{\text{N}}{2}, \text{ or } 0.5 \text{ N}\right)$, etc., solutions are often used.

168. Nomenclature of Acids. — Acids consisting of two elements are called **binary** acids. They are designated by the names of *both* elements. Thus HBr is *hydrobromic* acid, and H_2S is *hydrosulphuric* acid.

The *anhydrous* compounds are named like ordinary compounds of two elements (*cf.* § 110); thus: hydrogen chloride, hydrogen sulphide, etc.

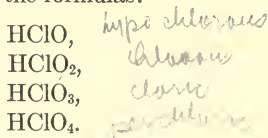
The salts of such acids are called chlorides, bromides, sulphides, etc. Thus, the sodium salt of hydriodic acid is called *sodium iodide*, and the barium salt of hydrochloric acid is *barium chloride*.

Most acids, however, are **ternary**, *i. e.*, consist of *three* elements: *Hydrogen, oxygen*, and a third element, which is usually a *non-metal*. Such are *nitric acid*, etc. These are given the name of the third element with the final syllable **ic**. This method of nomenclature applies, however, only to *inorganic* acids; *organic* acids, *e. g.*, acetic, tartaric, citric, picric, etc., acids are quite arbitrarily named.

When there are two acids containing the same three elements in different proportions, the ending

of the acid containing the smaller proportion of the oxygen is made *ous*, while the ending of the one containing more of this element is made *ic*. Thus, nitrogen forms with hydrogen and oxygen at least two compounds which are acids; of these the one containing the less oxygen — its formula is HNO_2 — is called *nitrous acid*, while the one containing the larger proportion of oxygen is called *nitric acid*. So sulphur forms with hydrogen and oxygen both *sulphurous acid*, H_2SO_3 , and *sulphuric acid*, H_2SO_4 .

The acids formed by the element chlorine, however, give the best illustrations of nomenclature. Chlorine forms with hydrogen and oxygen *four* acid compounds, the compositions of which are represented by the formulas: —



The second of these compounds, HClO_2 , is called *chlorous acid*; the third, *chloric acid*; the first, because it contains less oxygen than chlorous acid, is called *hypochlorous acid* ("hypo" signifies "under" or "lower than"); the fourth, because it has more oxygen than chloric acid, is called *perchloric acid*.

Ternary acids containing oxygen are also called *oxygen acids*, or *oxy-acids*.

169. Nomenclature of Salts. — The salt of an acid ending in *ous* is given the ending *ite*, the prefix *hypo* remaining unaltered, if present.

Thus, sodium salt of nitrous acid is sodium *nitrite*, NaNO_2 ; the potassium salt of chlorous acid is potassium *chlorite*, KClO_2 ; and the calcium salt of hypochlorous acid is calcium *hypochlorite*, $\text{Ca}(\text{OCl})_2$.

The salt of an acid ending in *ic* is given the suffix **ate**, the prefix *per* remaining unchanged, if present.

Thus, the ammonium salt of nitric acid is ammonium *nitrate*; the barium salt of chloric acid is barium *chlorate*, $\text{Ba}(\text{ClO}_3)_2$; the potassium salt of permanganic acid is potassium *permanganate*, KMnO_4 .

In many cases there are two salts of the same metal with a given acid, as, for example, two iron sulphates, designated by the formulas FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, respectively. To distinguish between these the ending of the name of the metal is changed to **ous** in the sulphate in which the metal has the *lower* valence and to **ic** in the case in which the metal has the *higher* valence.

Thus, FeSO_4 is called *ferrous* sulphate, just as FeCl_2 is called *ferrous* chloride (cf. § 111); and $\text{Fe}_2(\text{SO}_4)_3$ is called *ferric* sulphate, just as FeCl_3 is called *ferric* chloride.

170. Nomenclature of Bases. — The name of a basic hydroxide contains the names of all the elements of which the hydroxide is composed. The ending is **ide**, the radical **OH** being treated as an element. When there are two basic compounds of *hydroxyl* with the same metal, the metal ends in **ous** in the hydroxide in which it has the *lower* valence, and in **ic** in the hydroxide in which it has the *higher* valence.

Thus, we have *cuprous hydroxide*, $\text{Cu}_2(\text{OH})_2$, and *cupric hydroxide*, $\text{Cu}(\text{OH})_2$; also *ferrous hydroxide*, $\text{Fe}(\text{OH})_2$, and *ferric hydroxide*, $\text{Fe}(\text{OH})_3$.

171. Exercises.

1. What is formed when a solution of sodium hydroxide is neutralized by nitric acid? Barium hydroxide by sulphuric acid? Ammonium hydroxide by acetic acid?

2. Name the calcium salt of carbonic acid; the lead salt of hydrochloric acid; the potassium salt of chloric acid; the barium salt of hypochlorous acid; the sodium salt of chromic acid; the silver salt of hyponitrous acid.

3. 8 grams of sodium hydroxide are contained in 50 c.c. of a solution; how many grams would this be in every liter?

4. 112 grams of potassium hydroxide are required to neutralize all the hydrochloric acid in a solution; how much of the acid was there? If the solution were evaporated, what salt would be found? How many grams of it?

5. What is the formula of the acid salt formed by sodium hydroxide and sulphurous acid? Its name?

6. 49 grams of sulphuric acid were required to redden litmus in a solution of potassium hydroxide; how much hydroxide was there in solution? How much potassium sulphate was formed?

7. What are the formulas of the basic chlorides theoretically possible from a consideration of the formula $\text{Bi}(\text{OH})_3$?

8. How many grams of solute to the liter are there in normal solutions of the following: KCl , BaCl_2 , $2 \text{H}_2\text{O}$, AgNO_3 , H_3PO_4 , $\text{Al}_2(\text{SO}_4)_3$, NH_4Cl , Na_2CO_3 ?

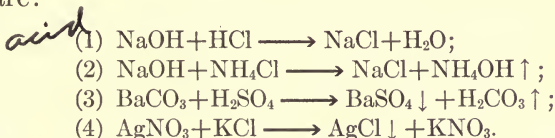
9. It takes 6.3 c.c. of normal sodium hydroxide to neutralize the sulphuric acid in 20 c.c. of a certain solution. How much sulphuric acid is present? Give its concentration in terms of a normal solution.

49
 49
 1000
 63

CHAPTER XV.

IONIZATION.

172. Double Decomposition of Acids, Bases, and Salts. — By far the most common reactions that take place in solution are those of double decomposition (*cf.* § 92). The essential thing about a double decomposition is that the two reacting substances behave as though they were broken up into two *kinds* of parts: An acid into *hydrogen* and an *acid radical*; a base, into *hydroxyl* and a *metal*; a salt, into a *metal* and an *acid radical*. The *reaction* consists in the **exchange** of these parts. Illustrations are: —



The double decomposition reactions of acids, bases, and salts, together with the physical properties of their solutions, have given rise to a theory that they are actually **dissociated in solution** (*cf.* § 175).

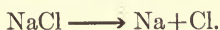
173. The Freezing Points, Etc., of Solutions. — In § 147 we learned that if gram-molecular weights of two substances, *e. g.*, glycerine and alcohol, are

each dissolved in 1,000 grams of water, the freezing points of the solutions are the same, viz.: -1.89°C . This does **not** apply to acids, bases, and salts. The freezing-point depression for 58.5 g. of sodium chloride in 1,000 g. of water is not 1.89°C ., but **more**. In dilute solution the depression is practically **twice** what we should expect. If the freezing point depression depends on the concentration of the molecules present, then the molecule of sodium chloride must be *dissociated into two particles*, each of which acts like a molecule in lowering the freezing point. A study of the boiling point and of the osmotic pressure of salt solution leads to the same conclusion. Acids, bases, and salts behave, in general, like common salt.

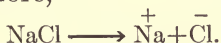
174. Electric Conductance of Solutions. — If an electric current is passed through dilute sulphuric acid, the water is *electrolyzed* (cf. § 61). Pure water does not conduct the current. Water containing HCl , NaCl , NaOH , KNO_3 , etc., conducts as well as dilute sulphuric acid. But if water contains glycerine, sugar, etc., it does **not** conduct readily. In electric conductance, then, as in double decomposition, the rule is that acids, bases, and salts are active, while other substances are not. A solution that conducts is called an **electrolyte**; one that does not, a **non-electrolyte**. Solutions of acids, bases, and salts are *not electrolytes for all solvents*; hydrogen

chloride dissolved in **toluene** (*cf.* § 524) forms a non-electrolyte.

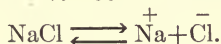
175. Theory of Dissociation in Solution. — Because of the peculiar behavior of electrolytes, Arrhenius developed the modern theory of solutions (1887). He considered that when salt is dissolved in water, it is separated into particles, called **ions**.



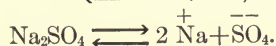
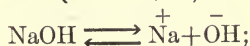
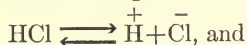
The solute is called an **ionogen**, i. e., ion-producer. In the electrolysis of salt solution, the sodium goes to the kathode (— electrode, *cf.* § 61); hence it is assumed that sodium ions carry + charges. The ions of *chlorine*, which go to the anode, are *negatively* charged. The **ionic equation** for the dissociation of salt is, therefore, —



But while water permits (or causes) the salt to be *ionized*, the two kinds of ions, since they have + and — charges, respectively, *reunite to form molecular salt*. Hence dissociation and recombination **balance** each other (*cf.* §§ 73 and 244).



For the dissociation of hydrochloric acid, sodium hydroxide, and sodium sulphate the equations are, —



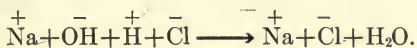
The total number of + charges is equal to the total of - charges, and *the number of charges carried by the ion is equal to its valence as an atom or radical* (cf. § 135). *Hydrogen and metals form + ions, or kations; non-metals, acid radicals, and hydroxyl form - ions, or anions.*

Relation of Ions to Atoms and Molecules. — The ions are not *atoms*; neither have they all the properties of molecules. They act like molecules, however, in their effect on the freezing point, etc., of solutions. If we ask why sodium in the ionic form is supposed to remain in water *without reacting with the water* (cf. § 74), the answer is, that the sodium atoms (or molecules) are *not free*, but *carry very large electric charges*, which completely change their behavior. So, *yellow* phosphorus, because it possesses more energy, has properties different from those of the *red* form (cf. § 345). When the charges on the ions of sodium are neutralized, they become ordinary sodium, and at once react with water.

176. Explanation of Neutralization. — A very simple explanation of the properties of acids, bases, and salts, and of *neutralization*, follows from the ionization theory. All *acids* in aqueous solution affect litmus in the same way because they all give *hydrogen ions* (H^+). The turning of litmus *red* is simply an indication of the presence of these ions. Similarly, *bases* are substances whose solutions contain hydroxyl (OH^-) ions.

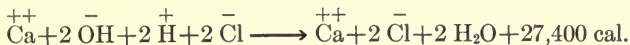
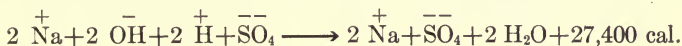
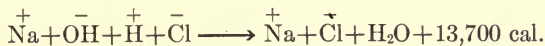
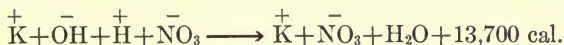
Neutralization is thus essentially the union of hydrogen and hydroxyl ions to form undissociated molecules of water.

The *ionic equation* for the neutralization of sodium hydroxide by hydrochloric acid is,—



When the water is removed, the sodium and chlorine ions unite to give *molecular* sodium chloride.

177. Heat of Neutralization. — The ionic view of neutralization is supported by the fact that the *amounts of heat evolved* when **normal** solutions (cf. § 167) of the strong acids are neutralized by a given base, such as sodium hydroxide, *are equal*, namely, **13,700 calories**. The same amount of heat is given off when other strong bases, such as potassium and calcium hydroxides, are used. The ionic equations showing this are: —



The equations show that the heat of neutralization is simply the heat evolved by the union of 1 g. of ionic H with 17 g. of ionic OH to form 18 g. of water.

178. Degree of Ionization.

Since it is the solvent that causes dissociation, dilute solutions should be better conductors than concentrated ones. This

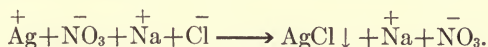
is the case. From measurements of the conductivity of sulphuric acid it has been calculated that the *concentrated* acid is only 0.7% ionized, *i. e.*, only 7 molecules in every 1,000, while a *normal* solution of the acid is 51% ionized. Similarly, concentrated (62%) nitric acid is only 9.6% ionized, but the normal solution, 82%. The *increase* in the ionization of strong acids, strong bases, and salts with increasing dilution finally stops, hence we conclude that at *great* dilutions the separation of the molecules into ions is complete. The acids and bases that are highly ionized at ordinary concentrations are chemically **active**; hence they are called “strong” acids and bases. “Strong” must not be confused with “concentrated” (*cf.* § 79). The degree of ionization for several substances is given in the following table: —

SUBSTANCE.	PER CENT IONIZED.	SUBSTANCE.	PER CENT IONIZED.
Hydrochloric acid. (Conc.)	13.6	Potassium chloride. N.	75.
Hydrochloric acid. N.	78.4	Potassium chlorate. N.	79.
Acetic acid. N.	0.4	Ammonium chloride. N.	74.
Carbonic acid. 0.1N.	0.17	Sodium chloride. N.	67.
Potassium hydroxide. N.	77.	Sodium chloride. 0.1N.	84.
Sodium hydroxide. N.	73.	Potassium sulphate. N.	53.
Ammonium hydroxide. N.	0.4	Potassium nitrate. N.	64.

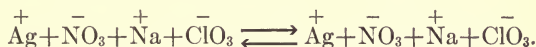
The ionization of water is very slight: the resistance a current encounters in passing through a layer of water 1 mm. thick is greater than that of a mercury column of the same cross-section and 66,000 miles long.

179. “Test” Reactions are Ionic. — When we “test” for metals or acid radicals, in solution, we are generally testing for **ions**. Thus, the test for a *chloride* (*cf.* § 130) is that it gives a *white* precipitate

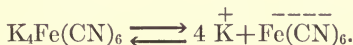
with silver nitrate solution, and that the precipitate is not affected by dilute nitric acid. We use the silver nitrate for its *silver ions*; these unite with *chlorine ions* to give *silver chloride*, which is insoluble.



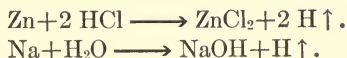
If, however, we add silver nitrate solution to a dilute solution of a *chlorate*, e. g., NaClO_3 , we do not get a precipitate of silver chloride, *because no chlorine ions are present*. The chlorine of sodium chlorate is part of the ion ClO_3^- . *Silver chlorate*, which might be formed, is not precipitated because soluble. Hence *no result is apparent*.



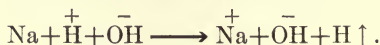
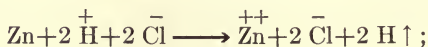
Another illustration: *Ferrous chloride*, FeCl_2 , gives with *ammonium sulphide* $(\text{NH}_4)_2\text{S}$, a black precipitate of *ferrous sulphide*, FeS ; but ammonium sulphide does *not* precipitate the iron of *potassium ferrocyanide* solution, $\text{K}_4\text{Fe}(\text{CN})_6$, *because iron ions are not present*.



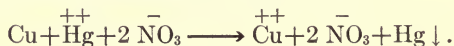
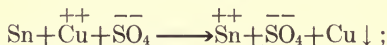
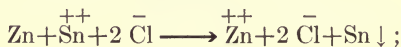
180. Replacement; the Electromotive Series. — When metals react with acids and with water to produce hydrogen (cf. §§ 57 and 74), the reactions are cases of *replacement* (cf. § 92).



From the **ionic** point of view, these equations are,

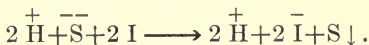
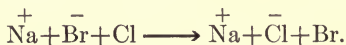


According to the equations, the reactions consist in the transfer of the + charges of the ionic hydrogen to the metals. Some metals, e. g., *silver*, cannot transfer their charges to hydrogen in this way, hence they do not react with acids to liberate hydrogen. A metal may replace, not only ionic hydrogen, but the ions of another metal: —



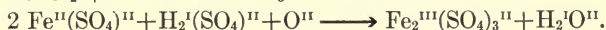
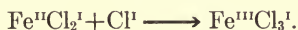
The metals and hydrogen may thus be placed in a *series*, called the **electromotive series** (*cf.* Appendix x), in which the metals coming first replace those that succeed them, from the solutions of their salts.

One **non-metal** may also replace another (*cf.* §§ 319 and 325) by the transfer of — charges: —

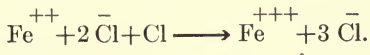


181. Oxidation and Reduction of Ions. — In § 138 we learned that an element may have different

valences in different series of compounds. Thus, iron is *bivalent* in ferrous compounds, such as FeO, FeCl₂, and FeSO₄, but *trivalent* in the ferric compounds, Fe₂O₃, FeCl₃, and Fe₂(SO₄)₃. So manganese is *bivalent* in MnO and MnCl₂, and *quadrivalent* in MnO₂ and MnCl₄. Now, to change FeO to Fe₂O₃ is to **oxidize** it (*cf.* § 25); oxidation is possible because iron can *increase its valence* from 2 to 3. On the other hand, Fe₂O₃ can be **reduced** to FeO because the valence of iron can fall from 3 to 2. For exactly the same reasons that apply to the oxides, ferrous **chloride** is said to be *oxidized* when changed to ferric **chloride**, and ferric chloride is said to be *reduced* to ferrous chloride, even though it is *chlorine*, and **not oxygen**, that is added or taken away. The test applied is that in *oxidation the valence is increased*, while in *reduction it is decreased*. In the following oxidation equations *valence symbols* (*cf.* § 133) are used: —

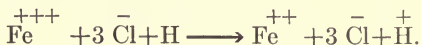


We have seen (*cf.* § 175) that the *number of charges* carried by an atom (or radical) acting as an ion *corresponds to the valence*. Accordingly, we may represent the oxidation of FeCl₂ to FeCl₃, in solution, by the *ionic equation*, —



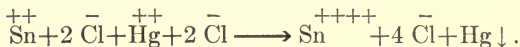
From the ionic point of view the oxidation of Fe^{II} to Fe^{III} consists in the taking up of an additional + charge by the ferrous ion. The iron is *oxidized*, because the chlorine becomes ionic, *i. e.*, it assumes a *negative* charge.

For the reduction of FeCl_3 by *nascent* hydrogen the ionic equation is: —



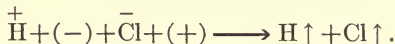
The iron is *reduced* because the hydrogen becomes ionic, *i. e.*, it assumes a + charge.

Ionic oxidation and reduction are well shown in the equation for the reaction between solutions of *stannous* (tin) *chloride* and *mercuric chloride* (*cf.* § 516).



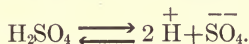
182. Electrolysis. — From the ionic point of view electrolysis of aqueous solutions is *not* the breaking up of the ionogen by the electric current: its molecules are dissociated by the *solvent*. The battery keeps the electrodes charged, and the ions move toward the electrodes; positive ions to the *kathode* (*cf.* § 61), and negative ions to the *anode*. The neutralization of their charges by the electrodes converts the ionic substances into ordinary, uncharged materials, which either escape, or react with the solution (or electrode) according to their properties.

Electrolysis of Acids. — The electrolysis of *hydrochloric acid* (cf. § 128) gives hydrogen and chlorine. In the equation, the charge received from the electrode is put in parenthesis: —

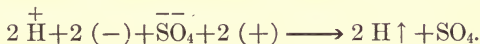


Here the **primary products** of the electrolysis are set free *without further change*.

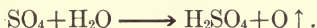
Dilute sulphuric acid is ionized according to the equation, —



For its *electrolysis* the equation is, —

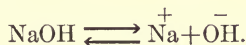


The hydrogen escapes, but the SO_4 reacts with the water: —

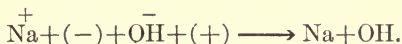


Hence the primary product SO_4 is converted into the *secondary* products $\text{H}_2\text{SO}_4 + \text{O}$. Sulphuric acid is thus *regenerated*: it is the water that is decomposed.

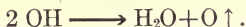
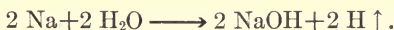
Electrolysis of Bases. — Sodium hydroxide solution is ionized according to the equation, —



The electrolysis equation is, —

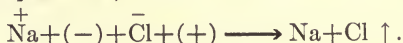


Each of the primary products undergoes change: —



Hence sodium hydroxide is regenerated at the kathode.

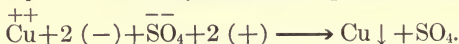
Electrolysis of Salts. — When fused *sodium chloride* is electrolyzed the equation is, —



In the electrolysis of an *aqueous solution* the metal acts upon the water, giving sodium hydroxide and hydrogen.

Sodium sulphate solution gives, as we may expect, sodium and SO_4 as *primary* products, while the secondary products are sodium hydroxide and hydrogen at the kathode, and sulphuric acid and oxygen at the anode.

Cupric sulphate is electrolyzed according to the equation, —



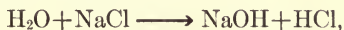
Copper is deposited upon the kathode, while SO_4 reacts with water, giving $\text{H}_2\text{SO}_4 + \text{O}$ at the anode.

183. Electro-chemical Equivalents.

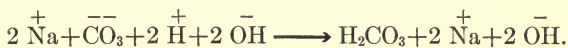
When *equal quantities* of electricity are passed through any two acids, such as hydrochloric acid and sulphuric acid, *equal weights* of hydrogen are liberated. Moreover, when hydrochloric acid is electrolyzed, hydrogen and chlorine are obtained in **equivalent** amounts, by weight (*cf.* § 76), *i. e.*, 1.008 grams of hydrogen for 35.45 grams of chlorine. In the electrolysis of *water*, hydrogen and oxygen are also obtained in equivalent weights, *viz.*, 1.008 : 8. The same current that liberates 1.008 grams of hydrogen from sulphuric acid will set free 31.8 grams of copper and 8 grams of oxygen from cupric sulphate, and 107.94 grams of silver from silver nitrate solution. The equivalent weights obtained by electrolysis are thus the same as those found from combination.

184. Hydrolysis. — When sodium hydroxide is neutralized by hydrochloric acid, the union of $\overset{+}{\text{H}} + \overset{-}{\text{OH}}$ to give molecular water is all but *complete*, because,

(1) the water is very slightly ionized (*cf.* § 178), and
 (2) the base and acid are both *strong*, i. e., highly dissociated, so that all their OH^- and H^+ can unite. Hence the *reverse* action, —



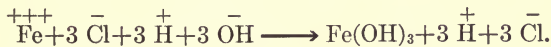
is very small. But when a salt formed from a *strong* base and a *weak* acid, e. g., *sodium carbonate*, is dissolved in water, the action of the ions of water is sufficient to give the solution a strongly *alkaline* reaction.



The action of the ions of water is called hydrolysis.

The cause for the hydrolysis of sodium carbonate is that the carbonic acid is *weak*, i. e., slightly dissociated into ions. The union of H^+ from the water with CO_3^{--} from the sodium carbonate, to give molecular H_2CO_3 , leaves an excess of OH^- in the solution.

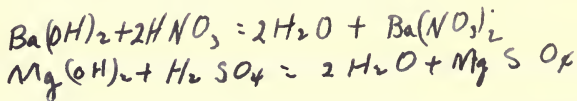
A salt of a *weak* base and a *strong* acid, e. g., *ferric chloride*, is also hydrolyzed; only in this case free acid, i. e., *ionic hydrogen*, is produced.



A salt of a weak base and a weak acid cannot exist in the presence of water: it is *completely* hydrolyzed (*cf.* § 478). The same is true of compounds like PCl_3 (*cf.* § 321). Here *two acids* are formed.

185. Exercises.

1. Define acid, base, and salt in terms of the ionic theory.
2. Write the ionic equations for the following reactions: hydrobromic acid and potassium hydroxide; barium hydroxide and nitric acid; magnesium hydroxide and sulphuric acid; sodium carbonate and calcium chloride.
3. Cold, concentrated sulphuric acid does not act with zinc to give hydrogen, but the dilute acid does. Explain.
4. If we include the ions of water, what *eight* substances are present in a solution of sodium chloride? Which are present in very small amounts?
5. The reaction of potassium cyanide and sodium phosphate (Na_2HPO_4) solutions is *alkaline*, and that of aluminum nitrate and cupric sulphate is *acid*. Write the ionic equations to "explain" this.
6. What is the color of anhydrous CuSO_4 ? Of SO_4 ions (recall the color of H_2SO_4 , Na_2SO_4 , etc.)? Of CuSO_4 solution? Of CuCl_2 and $\text{Cu}(\text{NO}_3)_2$ solutions? What is the common cause of the color of all three? Compare ordinary copper with ionic copper.
7. How would you change a *chlorate* into a *chloride*? What is the other product? How would you test for a *chloride*? How can you combine these tests to test for a *chlorate*?
8. From the table of **quantitative solubility** (Appendix viii) tell if it is possible to make solutions of silver nitrate and sodium chlorate of such a concentration that *silver chlorate* will be precipitated when the solutions are mixed. Is it possible for silver nitrate and *potassium chlorate*? Explain.



CHAPTER XVI.

NITROGEN AND THE ATMOSPHERE.

186. Existence of Nitrogen. — Nitrogen is found uncombined chiefly in air, of which it makes up about 78% by volume and 75.5% by weight. It is found combined with many elements, as with hydrogen in ammonia, and with hydrogen and oxygen in nitric acid. Nitrogen is an essential constituent of all animals and of many plants.

187. Preparation. — *Crude* nitrogen may be prepared from air by the removal of the oxygen by means of phosphorus or copper. With phosphorus the operation is as follows: —

A vessel (Fig. 40) of air is placed over a bit of burning phosphorus which is floated in a small dish upon water. The phosphorus unites with the oxygen in this confined portion of air to form phosphorus pentoxide, which is a white solid easily dissolved by the water. If the experiment is carried out accurately, the water which rises into the vessel after the experiment is a measure of the oxygen used up by the phosphorus.

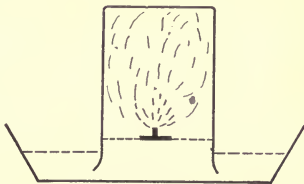


FIG. 40.

The oxygen of air is removed more satisfactorily by hot copper. The apparatus is shown in Fig. 41.

Pure nitrogen may be prepared by heating *ammonium nitrite*, NH_4NO_2 , or, better, a mixture of solutions of ammonium chloride

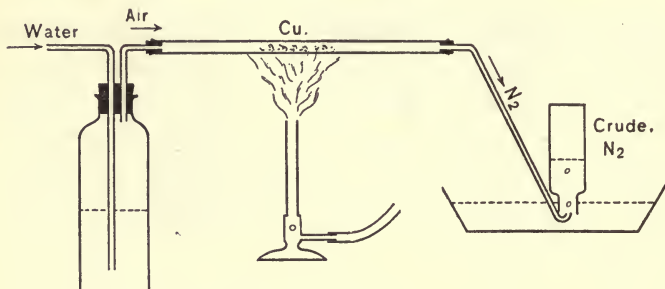
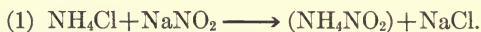


FIG. 41.

(NH_4Cl) and sodium nitrite (NaNO_2). When this mixture is heated, a regular stream of nitrogen is evolved.

The equations are: —



188. Properties of Nitrogen. — Pure nitrogen is a gas without taste, odor, or color, and about 0.97 as heavy as air. 100 c.c. of water under ordinary conditions can dissolve only about 1 c.c. of the gas. *One liter* of nitrogen weighs about 1.25 g. *under standard conditions*, i. e., at 0°C . and 760 mm. pressure.

Since ordinary combustion and respiration require oxygen, it naturally follows that "atmospheric nitrogen," *i. e.*, air deprived of oxygen, no longer supports either combustion or respiration. Pure nitrogen, like atmospheric nitrogen, is an extremely inactive substance, combining directly with only a few elements. It does combine with magnesium, titanium, lithium, etc., at an elevated temperature, giving **nitrides**, *e. g.*, Mg_3N_2 .

Under the influence of the electric spark, nitrogen unites with hydrogen and oxygen to form nitrous and nitric acids, and with hydrogen alone to form ammonia; hence these compounds, and the substances formed from them, *viz.*, *ammonium nitrite* and *ammonium nitrate*, are found in the atmosphere, in water, and in the soil.

Bacteria living on the roots of some plants, such as peas and clover, can take up nitrogen directly from the air, forming *albumins*.

189. "Atmospheric Nitrogen" a Mixture.—Careful experiment shows that a liter of atmospheric nitrogen weighs 1.2571 grams and one of pure nitrogen 1.2507 grams. The cause of this difference is that atmospheric nitrogen contains another substance, heavier than nitrogen. Thus *argon* was discovered in 1894.

190. Character of the Atmosphere.—The atmosphere is the gaseous mantle of the earth. Some of

its ingredients are practically *constant* in amount, but others are *variable*.

Constant Ingredients.	Variable Ingredients.
Nitrogen,	Water,
Oxygen,	Carbon dioxide,
Argon,	Ozone,
Helium,	Hydrogen peroxide,
Hydrogen, &	Ammonium nitrite,
and several rare and recently	Dust,
discovered substances.	etc.

Bacteria are so universally present and of such great importance to many changes taking place in the atmosphere that they may rightly be classed among its variable ingredients.

By *pure* air we mean a mixture of the constant constituents of the atmosphere. The proportions, by volume and by weight, of the three most abundant of these are as follows: —

BY VOLUME.	BY WEIGHT.
Nitrogen, 78.06%	75.5%
Oxygen, 21.00%	23.2%
Argon, 0.94%	1.3%

Hydrogen exists in small quantities in the atmosphere: 100 liters of it contain about 19 c.c. of hydrogen. Hydrogen is thus present in almost as great an amount by volume as carbon dioxide (*cf.* § 193).

Nitrogen and oxygen, the most abundant constituents of air, have been described already. The *rare gases* of the atmosphere include argon, helium, neon, krypton, and xenon. These form a *natural family* (*cf.* § 377). All are inert, and have a valence of 0.

191. Argon. — The discovery of argon *almost* took place a hundred years before this substance was actually studied by Ramsay and Rayleigh in 1894; for Cavendish, the discoverer of hydrogen, records the observation that he could not get all the nitrogen of the air to combine with oxygen by “sparking” a mixture of these gases in the presence of potassium hydroxide. This was in 1785. The “residual nitrogen” was argon and the other inert gases which are mixed with atmospheric nitrogen. By repeating Cavendish’s experiments, Ramsay and Rayleigh obtained argon.

A second way of obtaining this substance is to pass pure air over heated copper, which takes up the oxygen, and then over magnesium, which absorbs the nitrogen as *magnesium nitride*, Mg_3N_2 . The nitrogen may also be removed by lithium or calcium.

Argon may be condensed to a colorless liquid, boiling at -185°C. , and at lower temperatures may even be obtained in the solid state. In gaseous form it is heavier than oxygen. It is much more soluble in water than nitrogen, hence in air which has been dissolved in water and afterward expelled from solution the proportion of argon is greater than in the atmosphere. Argon is *almost without chemical activity*, hence its name.

192. Helium. — By means of the spectroscope, helium was discovered to be a constituent of the sun

a quarter of a century before it was known to exist on the earth. It has been found in small amount in the earth's atmosphere, in certain rare minerals, in some springs, and in a meteorite, as well as in the atmospheres of the sun and certain fixed stars. Like argon, helium is very inert. *It is probably less soluble in water than any other gas.*

193. Carbon Dioxide in the Atmosphere. — The chief *variable* constituents of the atmosphere are carbon dioxide and steam, and to the presence of these two substances many of the properties of the atmosphere are due. The atmosphere supports the life of chlorophyll-producing plants largely because it contains carbon dioxide.

The presence of carbon dioxide in the atmosphere may be shown by drawing a current of ordinary air through a solution of calcium hydroxide (lime-water); the white solid which separates from solution is calcium carbonate, CaCO_3 (*cf.* § 283).

Under ordinary conditions, 10,000 parts, by volume, of air contain only 3 or 4 parts of carbon dioxide. Expired air contains 4%. If the air of a room contains 8 to 10 parts in 10,000, it is unfit to breathe, both because of the carbon dioxide itself and of the decaying organic matter which is always exhaled along with it from the lungs. The quantity of carbon dioxide in the atmosphere of a room thus serves as an *index* to the amount of poisonous material present.

The great weight of the earth's atmosphere may be illustrated by the fact that its carbon dioxide, although so small a proportion of the whole, is estimated to weigh over five million millions of tons.

194. Water Vapor in the Atmosphere. — The quantity of water vapor which the atmosphere is capable of holding at any given time depends upon the temperature and the pressure. *Air is saturated with water vapor*, or at the "*dew-point*," when the *slightest reduction* of temperature or *increase* of pressure causes *precipitation* of some of the water.

One hundred liters of air at 25° C. and at ordinary pressures can hold a little over 2 grams of water. If the temperature falls to 0° C., about 1.7 grams of the water are precipitated as rain. Usually the atmosphere is far from having all the water it can hold, only 60%, or less, of this amount being present on a fair day. If there is much more than this, we recognize its presence by the "closeness" of the atmosphere.

195. Atmospheric Dust. — The importance of atmospheric dust in causing certain phenomena is well known. It causes sunset and sunrise colors, and helps to effect the precipitation of water vapor as clouds and rain. An experiment to illustrate the latter influence is the following: —

A large flask (Fig. 42) is filled with dust-free air by drawing through it, for some hours, air which has passed through a long tube of cotton wool. If the room is now darkened, and a beam of light is directed through a small opening toward the flask, the beam will be visible in the outer air, but not in the flask, owing

to the absence of dust. A small amount of steam is next introduced into the flask by connecting the flask at *a* with a vessel of boiling water, opening the pinch clamps at *a* and *b*, and sucking for a moment with the aspirator. A beam of light, directed as before, will be practically invisible. The beam will still be invisible when the flask is connected with the aspirator and partly exhausted. A small funnel is now attached to the tube at *a*,

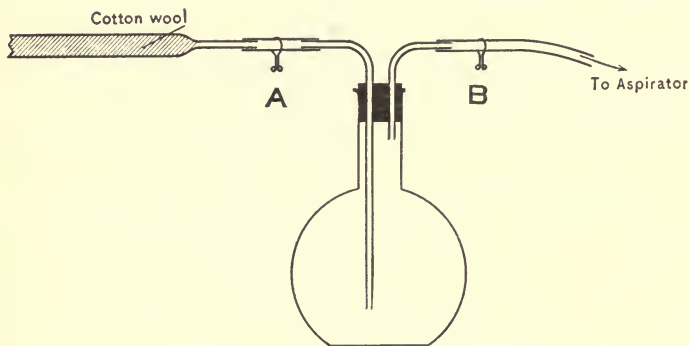


FIG. 42.

and a quantity of smoke is produced in the mouth of the funnel. This smoke is sucked into the large flask by opening the clamps at *a* and *b*, and thus making connection with the aspirator. If now the clamp *a* is closed, and the air is slightly exhausted through *b*, a beam of light passing through the flask will be clearly visible owing to the small drops of water, *i. e.*, mist, which fill the flask. In a similar way the dust of the air probably causes the formation of *drops* of water.

196. Weight and Pressure of the Atmosphere. —
One liter of air weighs, under standard conditions,

1.293 grams, and is, therefore, $\frac{1}{773}$ as heavy as water, and about 14.4 times as heavy as hydrogen. Because of its weight, the atmosphere exerts pressure upon all bodies immersed in it. This pressure is measured by the height of the column of mercury the atmosphere will support in the barometer (Fig. 9).

197. Liquefaction of Air. — The condensation of air to the liquid condition is brought about by the same methods as those used to liquefy other “permanent” gases, and differs radically from the liquefaction of gases like ammonia, chlorine, and sulphur dioxide. These gases may be condensed *at ordinary temperatures*, if only sufficient pressure is applied; but gases like air cannot be liquefied at the ordinary temperature *by any pressure, however great*. Pressures up to thousands of atmospheres have been applied without avail. This is due to the fact that there is for every gaseous substance a maximum temperature above which the gas *cannot* be liquefied; this is called the **critical** temperature of the gas.

A “permanent” gas thus differs from an easily condensable gas in this respect, viz., that the critical temperature of a condensable gas is *above* the ordinary temperature, while that of the permanent gas lies far *below* the ordinary temperature. Such gases as air, hydrogen, etc., are, therefore, condensed only at a very low temperature and great pressure.

Two general methods are used to liquefy true gases. In the *first* method the gas to be condensed is first

cooled to its critical temperature, and is then subjected to pressure. In the *second* method the gas is first strongly compressed, and is then cooled to its critical temperature. The second method has been used to liquefy air on a commercial scale.

The apparatus consists of two pipes, either straight or coiled, many yards long, the outer pipe forming a jacket about the inner one. The air is liquefied in the *inner* pipe. By means of compressing engines (Fig. 48) air is forced *through* the inner pipe at a pressure of about 200 atmospheres. Compressing the air **heats it**, but it is cooled to the ordinary temperature, by running water, before entering the liquefier. The compressed air is forced *out of* the inner tube, through a small opening controlled by a needle valve, into the outer tube. Here the pressure is low; it may be at one atmosphere. The compressed air thus **expands** greatly, and **becomes cold**; for the expanding gas takes up the heat given off when it was originally compressed. In the outer tube the cold, expanded air *passes back*, around the inner tube, *cooling* it. The cooling effect, upon the compressed air, of the gas escaping, say, each minute, is small, but each new portion of escaping gas is at a lower temperature than the last. The cooling effect due to each expansion also becomes greater as the temperature falls. Finally the compressed air is cooled to the temperature at which it liquefies, under the pressure used. The air escaping through the valve then contains drops of liquid air. These are caught in a part of the outer tube and drawn off into storage vessels (*cf.* Fig. 43).

198. Properties of Liquid Air. — In the liquid condition air is colorless, has about the same density as water, and boils at -190° C., under ordinary pres-

sure. When freshly made, liquid air is about half oxygen, but the proportion of oxygen increases by the evaporation of the nitrogen (liquid nitrogen boils about 10° C. below liquid oxygen) until the liquid is over 90% oxygen.

Liquid air is preserved in open, double-walled vessels called *Dewar bulbs* (Fig. 43). The space between the walls of the bulbs is exhausted of air to secure non-conductivity of heat. Tin or wooden boxes having double walls filled with silk may also be used.

Alcohol, liquid carbon dioxide, mercury, etc., solidify when placed in liquid air, and steel burns in it like tinder; yet the hand may be held in it for a short time without injury, because protected by a non-conducting film of air in the gaseous state.

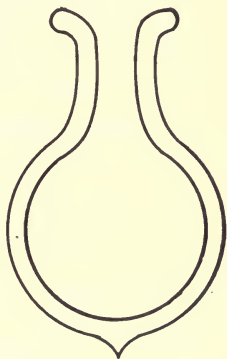


FIG. 43.

199. Determination of the Proportion of Oxygen in Air. — The amount of oxygen in a given volume of air is usually determined either (1) by absorbing the oxygen, or (2) by exploding the air with a known volume of hydrogen.

The *phosphorus absorption method*, a crude form of which was described under nitrogen (*cf.* § 187), is carried out more accurately as follows: —

A gas analysis tube, partly full of air, is inverted in a hydrometer jar (Fig. 5), and the gas volume is carefully measured. The

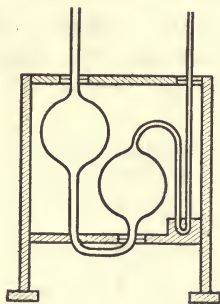


FIG. 44.

temperature and pressure are recorded. A thin stick of phosphorus is introduced into the tube by means of a bent wire, and is left there twenty-four hours. The phosphorus is then removed, and the residual gas is measured. When the necessary corrections have been made, the volume of oxygen absorbed and its per cent of the original air are readily calculated.

The oxygen may also be absorbed by *potassium pyrogallate* (cf. § 549) in a Hempel pipette (Fig. 44).

The second general method, viz., the explosion of a mixture of known volumes of air and hydrogen, may be illustrated as follows:—

In the straight eudiometer tube shown in Fig. 45, a known volume of air is mixed with an excess of hydrogen, and the electric spark is passed through the mixture. All of the oxygen of the air taken will thus unite with hydrogen to form water.

The volume of *steam* formed will be equal to that of the hydrogen used up, but the volume of *liquid* water produced by the condensation of the steam will be

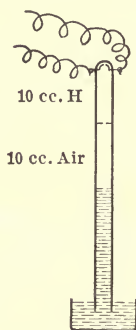


FIG. 45.

insignificant. Hence there will be a *contraction* of volume. One-third of this contraction will be the volume of oxygen present in the original air.

To take a concrete example: If 10 c.c. of each of the gases, air and hydrogen, are taken, the volume remaining after the explosion will be about 13.7 c.c., *i. e.*, the contraction will be 6.3 c.c. Of this contraction 2.1 c.c. ($=\frac{1}{3}$ of 6.3) are oxygen; hence 10 c.c. of air contain 2.1 c.c. ($=21\%$) of oxygen.

The proportions of the chief *constant* constituents of the atmosphere have been determined in many different places, and have been found everywhere practically the same. This is a remarkable fact when we remember that air is only a physical mixture, yet it is a necessary consequence of the circulation of the air and the rapid diffusion of its gases.

200. The Air a Physical Mixture. — That air is not a *compound* of nitrogen and oxygen is proved by several facts, of which the following are illustrations: —

(1) When nitrogen and oxygen are mixed, there is no evidence of union, such as evolution or absorption of heat, change of volume, etc.

(2) If air were a chemical compound, like the nitrogen oxides, it ought to have the same composition in the liquid state as in the gaseous. This, however, is not the case, as was stated in the description of liquid air.

(3) There is no reason why air, if a compound, should have its composition changed by solution in water; yet this is the case.

Air that has been expelled from solution in water contains about 35%, by weight, of oxygen, instead of 23%, owing to the fact that oxygen is much more soluble than nitrogen.

201. Exercises.

1. Calculate the percentage composition of a mixture of gases, if 76 c.c. of the mixture contain 48 c.c. oxygen, 12.5 c.c. hydrogen, and the remainder nitrogen.

2. Why is not all the carbon dioxide at the earth's surface? If it were, how deep a layer, in feet, would there be? (Cf. §§ 193 and 278.)

3. It has been calculated that 900 grams of nitric acid fall every year upon an acre of ground. Can you suggest how it was formed?

4. 16 c.c. of a mixture of nitrogen and oxygen were put with 25 c.c. of pure hydrogen, and exploded. The residual gas had a volume of 23 c.c. How much of the original mixture was oxygen?

5. How many liters of air are there in a room 3 m. high, and 5 m. square? How much does it weigh at 20° C. and 740 mm.? How much of it is oxygen? How much of it is argon? How much is carbon dioxide?

6. Explain why liquid air becomes more and more blue on standing.

7. 20 liters of air at 15° C. and 730 mm. were passed through lime-water, and the calcium carbonate (CaCO_3) formed weighed 0.0256 gram. How many c.c. of CO_2 were there in the 20 liters of air?

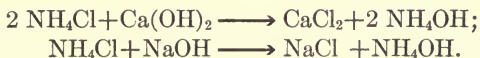
CHAPTER XVII.

AMMONIA.

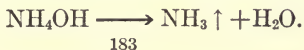
202. Occurrence. — Ammonia is formed in nature by the decay of organic compounds containing nitrogen, and by electric discharges in moist air (*cf.* § 188), consequently ammonia and ammonium compounds occur in the atmosphere, in rain water, and in the soil. Small amounts of ammonium compounds are found in plants and in animal secretions.

203. Laboratory Method of Preparation. — In the laboratory, ammonia is made, either (1) by *heating an ammonium salt with a base*, or (2) by *warming concentrated ammonium hydroxide solution*.

The ammonium salt in method (1) is usually the chloride or sulphate. The base is generally slaked lime $[\text{Ca}(\text{OH})_2]$, or powdered sodium hydroxide. "Soda-lime," a mixture of sodium hydroxide and quicklime, is also used. The equations for the double decomposition are:



Ammonium hydroxide is *unstable*, and breaks up readily into ammonia and water:



The **first method** of preparing ammonia may be carried out by mixing about equal parts, by weight, of ammonium chloride

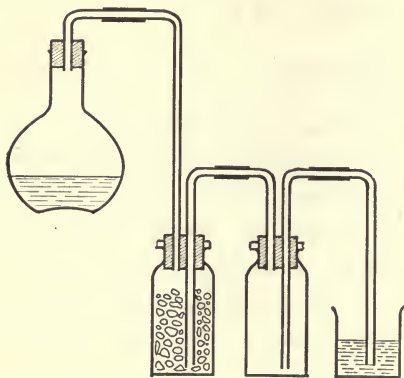


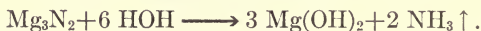
FIG. 46.

and dry calcium hydroxide (or "soda-lime") in a flask (Fig. 46), and heating the flask gently. If the gas is wanted *dry*, it is passed through a bottle, or U-tube, of quicklime or of coarsely broken sodium hydroxide. Calcium chloride may not be used, because ammonia combines with it to give a crystalline compound, $\text{CaCl}_2 \cdot 8 \text{NH}_3$. Since water com-

combined in this way is "water of crystallization," the ammonia of the compound may be described as "ammonia of crystallization." As in the case of chlorine and hydrogen chloride (§§ 114 and 126), we can tell when the gas of the collecting bottle (the "empty" one in the figure) is free from air by passing it *through* this bottle into a solvent (here, water), until the bubbles of gas are completely taken up by the solvent.

The **second method** of making ammonia is to heat concentrated "ammonia water." Much ammonia is evolved. It may be dried as already described.

Ammonia from Nitrides. — Ammonia is also formed by the hydrolysis (*cf.* § 184) of many *nitrides* (§ 188), *e. g.*, Mg_3N_2 : —



204. — Commercial Sources of Ammonia. — The two chief sources of ammonia are:

(1) The *dry distillation of animal matter* (bones, skin-products, etc.).

(2) The *dry distillation of soft coal*.

Formerly all ammonia and all ammonium compounds were made by the *dry distillation* of animal matter; hence the name "spirits of hartshorn," "*spirit*" meaning a distillate, and "*hart*" being a general term for "deer," etc. The horns, bones, hoofs, hides, hair, etc., of animals contain nitrogenous bodies, which give much ammonia when heated with quicklime without access of air.

This method is used in many places, especially since the old method of making illuminating gas has been abandoned, to convert into a valuable product almost worthless scraps of animal matter.

The *most common source* of ammonia for many years has been the wash liquors of the gas works. Gas is made in the **old process** by the *dry distillation of soft coal* (cf. § 297). At first it contains many impurities, among them ammonia, hydrogen sulphide, and carbon dioxide; these are removed by passing the gas through water. When the wash water, containing ammonium sulphide, ammonium carbonate, etc., is heated with slaked lime, ammonia gas is evolved.

Ammonia comes into the market as ammonia water (ammonium hydroxide) and also in the liquid state.

205. Physical Properties. — Ammonia is a colorless gas of characteristic odor. One liter of it under

standard conditions weighs 0.762 gram; ammonia is therefore 0.59 as heavy as air.

Ammonia gas is *very* soluble in water: 1 c.c. of water absorbs, under standard conditions, 1,146 c.c. or 0.873 gram of the gas. The specific gravity of a 35% solution at 15° C. is about 0.88; that of the so-called 28° Beaumé solution is about 0.90.

Dry ammonia rushes into cold water as into a vacuum, and is likewise very soluble in alcohol and in ether. Charcoal can take up under favorable conditions about ninety times its own volume of ammonia gas.

206. Liquefaction of Ammonia.—The critical temperature of ammonia is far above the ordinary

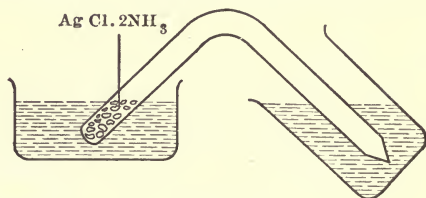


FIG. 47.

temperature, hence the gas may be liquefied by pressure. A simple apparatus for condensing ammonia is shown in Fig. 47.

A small amount of the compound which silver chloride forms with ammonia, viz., $\text{AgCl} \cdot 2\text{NH}_3$, is placed in the rounded end of the bent tube. The tube is then sealed, and the end containing the silver ammonium compound is warmed in a water bath, while the drawn-out end is cooled in a freezing mixture. The compound containing the ammonia is thus decomposed, and the ammonia is condensed in the drawn-out end.

Liquid ammonia is about 0.6 as heavy as water. It boils at -40°C . under ordinary pressure, and freezes at -75°C .

207. Liquid Ammonia as a Refrigerating Agent. — The chief use of liquid ammonia is as a refrigerating

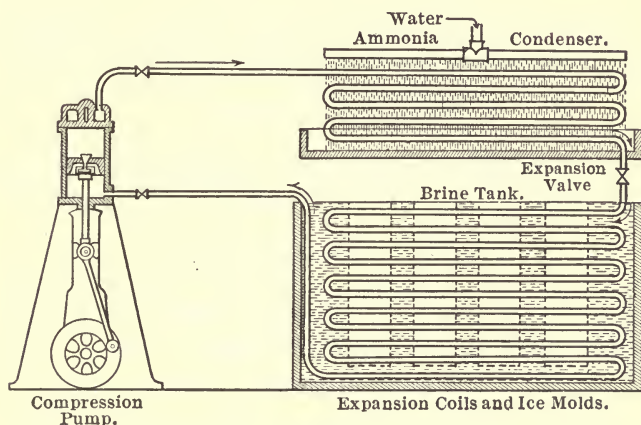


FIG. 48.

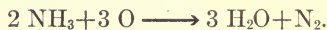
agent, and to produce artificial ice. For this purpose gaseous ammonia (produced by heating ammonia water) is condensed to the liquid state, and the liquid ammonia is then allowed to evaporate rapidly. The heat necessary for the vaporization of the ammonia is *absorbed from the body to be cooled*.

The apparatus shown in Fig. 48 gives, in principle, the construction of a refrigerating system.

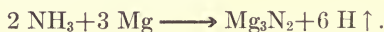
The compression engine forces gaseous ammonia into condensing pipes (cooled by streams of water) under so great a pressure that the ammonia is liquefied. The liquid ammonia is then allowed to expand in another system of pipes surrounded by a brine of concentrated salt solution or of calcium chloride solution. These may be cooled to -21° C. and -48° C., respectively, before they freeze. When tanks containing water are placed in the cold solutions, the water is frozen.

Instead of ammonia, liquid sulphur dioxide, liquid carbon dioxide, compressed air, etc., are often used to produce artificial ice.

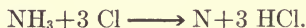
208. Chemical Properties. — Ammonia does not burn in the air, but it burns readily in oxygen.



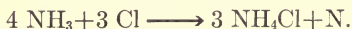
Ammonia reacts with heated magnesium, giving the *nitride* (*cf.* § 188) and hydrogen,—



Chlorine reacts energetically with ammonia, forming nitrogen and hydrogen chloride. The equation is, —



If the ammonia is present in excess, the hydrogen chloride unites with some of it, forming ammonium chloride. The complete equation is, therefore, —



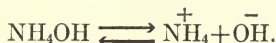
A similar reaction occurs between ammonia and bromine.

Gaseous ammonia and hydrogen chloride unite in equal proportions by volume to form solid ammonium chloride.

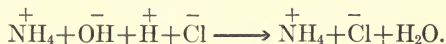
209. Ammonium Hydroxide. — When ammonia dissolves in water, the solution contains *ammonium hydroxide*: —



The hydroxide is ionized like any base (*cf.* § 175):

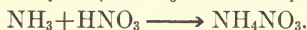
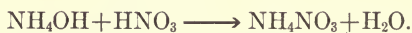


The conductivity of the solution is, however, very slight; hence we conclude that the concentration of $\text{NH}_4^+ + \text{OH}^-$ is very small. This may be due to the fact that ammonium hydroxide is not readily dissociated (weak base); or it may be that most of the ammonia is merely *dissolved in the water, but not combined with it*. When ammonium hydroxide is treated with a strong acid, the salt produced is *neutral*. Judged by this test, ammonium hydroxide is a **strong** base. The discrepancy is readily explained. When an acid is added, its H ions remove the OH ions present, consequently more ionization of molecular NH_4OH takes place. To keep up the supply of NH_4OH molecules, NH_3 and H_2O combine until all the NH_3 is used up. The solution then contains only the ammonium salt and its ions.



Because of its basic properties, ammonia water is used in cleaning, to remove grease and acids, and to soften water (*cf.* § 70).

210. Ammonium Salts. — Ammonium salts are made by the neutralization of the hydroxide by acids (*cf.* § 160), or by the direct union of ammonia with the acids, *e. g.*,—

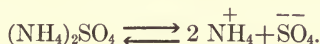
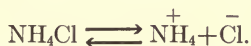


All the common ammonium salts are white, and form colorless solutions. The group NH_4 has not been obtained as a substance, because it breaks up into ammonia and hydrogen (*cf.* § 427); but, since its compounds are like those of the metals, it is called **ammonium** and is treated as a **metal radical** (*cf.* §§ 105 and 160). In ammonia the valence of the nitrogen is 3. In the ammonium compounds two univalent groups are added, raising the valence to 5. The accompanying table shows the resemblance between the formulas of ammonium compounds and those of sodium and potassium.

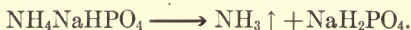
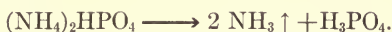
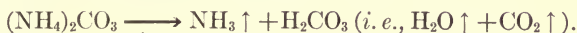
	AMMONIUM.	SODIUM.	POTASSIUM.
Chloride.	NH_4Cl	NaCl	KCl
Nitrate.	NH_4NO_3	NaNO_3	KNO_3
Sulphate.	$(\text{NH}_4)_2\text{SO}_4$	Na_2SO_4	K_2SO_4
Hydroxide.	NH_4OH	NaOH	KOH
Carbonate.	$(\text{NH}_4)_2\text{CO}_3$	Na_2CO_3	K_2CO_3
Phosphate.	$(\text{NH}_4)_3\text{PO}_4$	Na_3PO_4	K_3PO_4

211. Dissociation of Ammonium Compounds. —

In solution, ammonium salts are dissociated like those of the metals: —



Ammonium salts are also dissociated when heated, giving ammonia, on the one hand, and acids, or acid salts, on the other. See, however, *ammonium nitrate*, § 238.



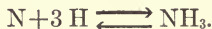
The temperature of dissociation varies greatly. For NH_4Cl , dissociation is complete above 350°C. ; hence, NH_4Cl does not exist, under ordinary pressure, above this temperature. When all the products of the dissociation are *volatile*, as in the case of ammonium chloride and carbonate, they **reunite** when they become sufficiently cool. Such salts are **sublimed** by heat. *Sublimation is the distillation of a solid.* When the acid (or acid salt) is *non-volatile*, as in the case of ammonium phosphate and ammonium sodium hydrogen phosphate, there is no sublimation; only the ammonia passes off (see § 357).

212. Composition of Ammonia. — Ammonia consists of nitrogen and hydrogen united in the proportion, **by weight**, of 14 parts nitrogen to 3 parts hydrogen. This fact is indicated by the formula NH_3 .

The **volumetric** composition of ammonia may be proved in several ways: —

- (1) By synthesis from nitrogen and hydrogen.
- (2) By the action of chlorine on ammonia.

213. Synthesis of Ammonia from Nitrogen and Hydrogen. — If the two gases, nitrogen and hydrogen, mixed in the proportion of 1 volume of nitrogen to 3 of hydrogen, are subjected to the electric discharge, they combine in part to form ammonia; the union cannot, however, be made *complete*, no matter how long the “sparking” is continued. This is due to the fact that a point is soon reached at which as much of the ammonia is decomposed in a given time as is formed in the same time by the union of nitrogen and hydrogen.



To make the combination complete, it is necessary to remove the ammonia *as fast as it is formed*.

This may be done by “sparking” the mixture of nitrogen and hydrogen over some substance, *e. g.*, sulphuric acid, capable of removing the ammonia.

It is thus proved that 1 volume of nitrogen unites with 3 volumes of hydrogen to form ammonia. The

union is accompanied by a *shrinkage in volume*, 4 volumes of the mixed gases becoming 2 volumes of ammonia (*cf.* § 140).

214. Action of Chlorine on Ammonia. — Since 1 volume of chlorine unites with 1 of hydrogen (*cf.* § 128), the relation of nitrogen to hydrogen can be obtained readily if that of nitrogen to chlorine can be established. For this purpose we make use of the known action of chlorine upon ammonia (*cf.* § 208). The experiment is carried out as follows: —

A Hoffmann tube (Fig. 49) is filled first with a saturated solution of sodium chloride in water, and then, by displacement of the salt solution, with chlorine.

The stopcock is then closed, and the cup above the stopcock is filled with concentrated ammonium hydroxide solution. The latter is now run, drop by drop, into the chlorine, care being taken that no air enters and no chlorine escapes. A flash of light will be seen when the first drops of ammonia water are introduced.

When almost all of the ammonia water has been run in, the stopcock is closed and the cup is filled with water. The cup is now connected, by means of a tube filled with water, with a beaker of dilute sulphuric acid, the stopcock is again opened, and the water and dilute acid are allowed to enter until the pressures inside and outside the tube are equalized.

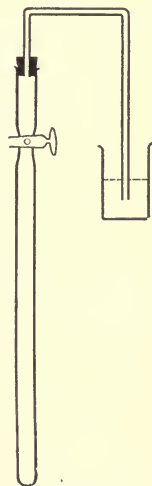


FIG. 49.

The tube, which was full of chlorine, will now be one-third full of nitrogen. Hence, —

Volume of nitrogen : volume of chlorine :: 1 : 3; whence

Volume of nitrogen : volume of hydrogen :: 1 : 3.

215. Exercises.

1. How many grams of ammonia can be made by heating 100 grams ammonium chloride with slaked lime? How many liters at 30° C. and 720 mm.?

2. What weight of ammonium sulphate is required to give, with lime, 20 liters of ammonia at 15° C. and 680 mm.?

3. What weight of slaked lime, Ca(OH)_2 , is necessary to decompose 50 grams ammonium nitrate? How many grams ammonia will be formed?

4. May concentrated sulphuric acid be used to dry ammonia gas? May phosphorus pentoxide? Why?

5. How could you separate a mixture of the gases ammonia, oxygen, hydrogen, and nitrogen so as to get the proportionate amounts of each in the mixture?

6. What would be the volume of each of the resulting gases if 500 c.c. of ammonia were completely decomposed into its constituents?

7. How many cubic centimeters of oxygen will be required to unite exactly with the hydrogen produced by the complete decomposition of 100 c.c. of ammonia?

8. Give the uses of ammonia, and tell upon what property each use depends.

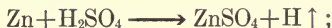
CHAPTER XVIII.

MOLECULAR FORMULAS AND EQUATIONS.

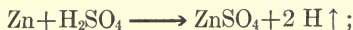
216. Molecular Equations. — In § 142 we learned that reasoning based upon Avogadro's hypothesis leads to the conclusion that the molecules of hydrogen, chlorine, oxygen, and nitrogen contain two atoms each. Now, in the free state these elements exist as *molecules*, not as atoms (*cf.* § 98). Hence, when the gaseous elements appear in equations, the *molecular formulas* (H_2 , Cl_2 , O_2 , and N_2) should be used. Equations containing the *molecular formulas of all the gases* in the reaction are called **molecular equations**. Some illustrations will show how molecular equations are evolved from the ordinary ones.

Thus, to form the molecular equation for the action of **zinc upon sulphuric acid**, —

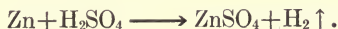
(1) We write the simplest possible equation, showing only the symbols and formulas of the materials used and produced: —



(2) We *balance* the equation: —

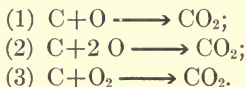


(3) Since free hydrogen exists as *molecules*, we write, —

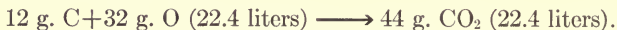


In this equation there is no comparison between the *volumes* of reagents or products, since only one, hydrogen, is a gas. However, since the formula H_2 represents a gram-molecular weight of hydrogen (2.016 g.), it also represents a gram-molecular volume, *i. e.*, **22.4 liters**, under standard conditions. From the molecular equation (3), therefore, we can make a direct comparison between the *weight* of zinc and sulphuric acid used, and the *volume* of hydrogen obtained: *65.4 g. zinc liberate 22.4 liters of hydrogen.*

As a *second* illustration we may take the **burning of carbon in oxygen**. The three equations are: —



Equation (3) shows that 1 volume of oxygen gives 1 volume of carbon dioxide; or, using the gram-molecular weights and volume, we read it thus: —



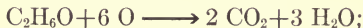
The carbon is not gaseous, hence its volume is not indicated.

The *third* illustration of molecular equations is the one for the **burning of alcohol vapor**: —

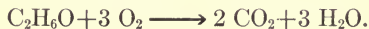
(1) The skeleton, or framework, of the equation: —



(2) The *balanced* equation: —



(3) The molecular equation: —



Since all molecules occupy the same space, this equation means that 1 volume of alcohol vapor + 3 volumes of oxygen (at the same temperature and pressure) give 2 volumes of carbon dioxide + 3 volumes of steam.

217. Determination of a Formula. — The simplest formula that can be assigned to a compound is determined from its percentage composition and the atomic weights of its elements. If the molecular weight of the compound can be obtained, we can decide whether the simplest formula is also the correct formula, or whether some multiple of the simplest formula must be taken. If the molecular weight cannot be found, we use the simplest formula. Some illustrations will explain the method.

Formula of Silicon Dioxide. — The percentage composition of silicon dioxide is, —

Si, 47.02%;
O, 52.98%.

This means that the weight of all the silicon atoms in the molecule of silicon dioxide is to the weight of all the oxygen atoms as 47.02 is to 52.98. Now, the *relative weights of the atoms* are represented by the *atomic weights*. Hence, if we divide the per cent of each element in the molecule of silicon dioxide by the atomic weight of the element, we get the *relative numbers of atoms* present.

$$\text{Relative number of Si atoms} = \frac{47.02}{28.4} = 1.655.$$

$$\text{Relative number of O atoms} = \frac{52.98}{16} = 3.31.$$

But there must be **whole**, not fractional, **numbers** of atoms in the molecule. We find that the ratio $\frac{1.655}{3.31}$ becomes $\frac{1}{2}$ if both terms are divided by the smaller, 1.655. Hence there are twice as many atoms of O as of Si, and the simplest formula is SiO_2 . As the molecular weight cannot be determined by the methods available (why?), this is the formula used.

Formula of Ethane. — Ethane is composed of carbon, 80%, and hydrogen, 20%. A liter of it weighs 1.34 g. under standard conditions. Find its formula. The relative number of carbon and hydrogen atoms is found by dividing the per cent of each by the atomic weight of the element.

$$\text{Relative number of C atoms} = \frac{80}{12} = 6.67.$$

$$\text{Relative number of H atoms} = \frac{20}{1} = 20.00.$$

The ratio $\frac{6.67}{20}$ becomes $\frac{1}{3}$ if we divide both terms by 6.67. Hence there are **3** hydrogen atoms in the ethane molecule for every carbon atom, and the *simplest formula* is CH_3 . The molecular weight of ethane, as found from the weight of 1 l. (cf. §§ 143 and 145), is **30**, while that corresponding to CH_3 would be 15; hence the simplest formula must be *doubled*. The formula of ethane is C_2H_6 .

Formula of Ether. — The composition of ether is: C, 64.86%; H, 13.51%; O, 21.62%. The vapor is 2.31 times as heavy as oxygen.

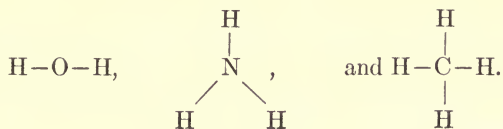
$$\text{Relative number of C atoms} = \frac{64.86}{12} = 5.405.$$

$$\text{Relative number of H atoms} = \frac{13.51}{1} = 13.51.$$

$$\text{Relative number of O atoms} = \frac{21.62}{16} = 1.35.$$

By dividing each of the three numbers by 1.35 we see that they are related as 4 : 10 : 1. The simplest formula of ether is, therefore, $\text{C}_4\text{H}_{10}\text{O}$. The molecular weight is about **74** (i. e., 2.31×32). This corresponds to that of the simplest formula.

218. Constitutional Formulas. — If we know the molecular formula of a compound, and the valence of its elements, we may represent the way in which the atoms are joined in the molecule by means of **constitutional**, or *structural*, **formulas**. When the molecules consist of *two* atoms each, as do those of hydrogen chloride and hydrogen, the atoms are assumed to be joined directly, and the constitutional formulas are $\text{H}-\text{Cl}$ and $\text{H}-\text{H}$. Here the combining power (valence) of each atom is represented by a single line, or **bond**. In the case of the water molecule we assume that the two hydrogen atoms are united to the one oxygen atom. The oxygen atom seems to have its power of holding other atoms directed along **two** lines, or *valences*, each of which can hold the single valence of a hydrogen atom. In the same way the nitrogen atom of ammonia is united with each of the *three* hydrogen atoms, and the carbon atom of marsh gas with each of the four carbon atoms (*cf.* § 132). The constitutional formulas of these substances are:—



219. Polymers.

Substances that have the same percentage composition, but different molecular weights, are said to be **polymers** of one an-

other. Thus, *formaldehyde*, *acetic acid*, and *grape sugar* have the **same** percentage composition: —

$$\text{C} = 40.00\%$$

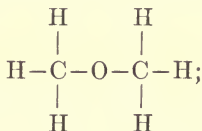
$$\text{H} = 6.67\%$$

$$\text{O} = 53.33\%$$

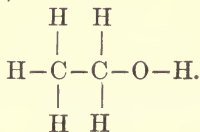
The *simplest* formula for each is, therefore, CH_2O . A substance having this formula must have a molecular weight of 30. This is the molecular weight of *formaldehyde*. The molecular weight of *acetic acid* is 60, and that of *grape sugar*, 180; hence these substances are the *di-polymer* and *hexa-polymer*, respectively, of formaldehyde, and their formulas are $\text{C}_2\text{H}_4\text{O}_2$ and $\text{C}_6\text{H}_{12}\text{O}_6$.

220. Isomers.

Many cases are known in which two or more compounds have the same composition and molecular weight, but different properties. Methyl ether and ethyl alcohol, for example, are both represented by the formula $\text{C}_2\text{H}_6\text{O}$; these substances are so different, however, that no one would mistake one for the other. Thus methyl ether boils at -24°C ., at ordinary pressure, while ethyl alcohol boils at $+78^\circ \text{C}$. Such compounds are said to be **isomers** of one another. Constitutional formulas represent the differences between isomers by *different arrangements of the atoms in the molecule*. Thus, the structural formula for **methyl ether** is,—



while that of alcohol is, —



According to these formulas, all the hydrogen atoms of methyl ether have the *same relation* to the remainder of the molecule and should behave in the same way with reagents; while in the case of ethyl alcohol *one* hydrogen atom — the one bound to oxygen — should be *different* from the other five. This is actually the case; for the atom of hydrogen bound to oxygen is the only one of the six that can be replaced by sodium and other metals.

221. Exercises.

1. Write the molecular equations for the following reactions: —

- (a) Union of hydrogen and chlorine.
- (b) Burning of hydrogen in air.
- (c) Union of nitrogen and hydrogen to give ammonia.
- (d) Action of sodium upon hydrogen chloride.
- (e) Burning of ethane in air.
- (f) Union of ammonia and hydrogen chloride.
- (g) Burning of ammonia in oxygen.
- (h) Decomposition of potassium chlorate by heat.
- (i) Reaction of zinc with hydrochloric acid.

2. A liter of a gas weighs 1.96 g. under standard conditions, and its composition is: C, 27.27%; O, 72.73%. Find its formula.

3. A certain gas consists of N, 63.64%; O, 36.36%. 200 c.c. of it weigh 0.3932 g. under standard conditions. What is its formula?

4. A certain compound has the composition: C, 52.17%; H, 13.04%; O, 34.78%. Its vapor is 1.44 times as heavy as oxygen. Find its formula.

5. A compound has the composition: C, 10.04%; H, 0.84%; Cl, 89.12%. 0.26 g. of it had a volume of 70 c.c. at 99° C. and under 740 mm. pressure. What is its formula?

6. A compound has a molecular weight of 72. Its composition is: C, 83.33%; H, 16.67%. Find its formula.

CHAPTER XIX.

NITROGEN ACIDS AND OXIDES.

222. Nitric Acid. — Nitric acid is one of the most important substances known to Chemistry. It has been in use since the time of the early alchemists, but its true nature was not understood until the latter part of the eighteenth century.

During the Middle Ages nitric acid was made by the distillation of a mixture of alum, blue vitriol, and niter.

Alum is potassium aluminum sulphate *plus* crystal water [$\text{K}_2\text{SO}_4, \text{Al}_2(\text{SO}_4)_3, 24 \text{ H}_2\text{O}$], and blue vitriol is cupric sulphate *plus* crystal-water ($\text{CuSO}_4, 5 \text{ H}_2\text{O}$); by the dry distillation of these substances sulphuric acid was set free. This with the niter (KNO_3) gave nitric acid.

223. Commercial Preparation. — At the present time nitric acid is made on a large scale by heating sodium nitrate with concentrated sulphuric acid. The operation is carried out in large iron retorts; and the vapors evolved are condensed in a system of glass tubes (Fig. 50). The resulting liquid is redistilled.

In this way there is obtained an acid of specific gravity 1.4; its boiling point is 120° to 121° C. This, the "commercial" grade of nitric acid, is only 68%, by weight, nitric acid. The remainder is water.

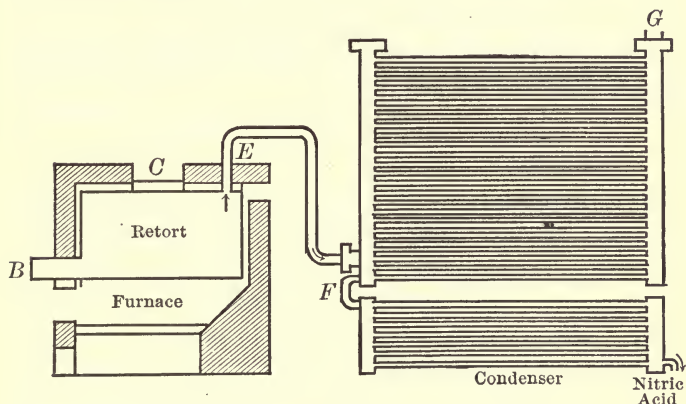


FIG. 50.

224. Laboratory Method.—In the laboratory, nitric acid is commonly made by heating potassium

nitrate with concentrated sulphuric acid in a retort or distilling bulb connected with a condenser. The condenser may be a flask kept cold by running water, as in Fig. 51.

When no more acid

distills over, the retort is allowed to cool; the other product of the reaction, potassium hydrogen sul-

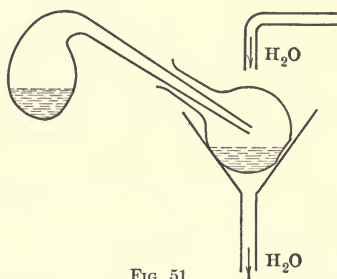
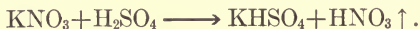


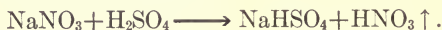
FIG. 51.

phate (KHSO_4), then crystallizes out in the form of long, white needles.

The equation for the reaction is, —



For the reaction between sodium nitrate and sulphuric acid the equation is, —



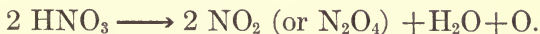
225. Preparation of Nitric Acid Compared with that of Hydrochloric Acid. — The preparation of nitric acid resembles that of hydrochloric acid. In each case the acid is set free from its salts by sulphuric acid, *not* because sulphuric acid is *stronger* than the acid it displaces, but because hydrogen chloride and nitric acid are *volatile*, and are, therefore, removed from the “field of action.” As a result, the reaction goes on until practically complete (*cf.* § 213).

In *each* of these cases only *half* of the hydrogen of sulphuric acid is replaced by the metallic element. If the temperature is raised considerably, a second portion of sodium nitrate will react with the sodium hydrogen sulphate formed, giving *normal* sodium sulphate and a second portion of nitric acid, according to the equation, —



In the treatment of sodium *chloride* with sulphuric acid on a commercial scale, this second reaction is actually carried out, because the compound Na_2SO_4 is wanted. In the preparation of nitric acid, however, the second reaction is of no advantage, since the high temperature necessary decomposes the nitric acid.

226. Properties of Nitric Acid. — Commercial nitric acid is dehydrated by distilling it with concentrated sulphuric acid. The anhydrous acid (the best yet made was probably 99.8% pure) is a thick, colorless oil of specific gravity 1.56. It begins to distill at 86° C., but is largely decomposed in the operation.



Under reduced pressure (*cf.* § 340) it distills undecomposed.

Nitrogen dioxide is a brown gas which dissolves readily in nitric acid; hence anhydrous nitric acid that has been distilled under ordinary pressure has a brown color. This color may be removed by bubbling air through the liquid.

The same decomposition of nitric acid takes place in the light (very rapidly in sunlight); hence the nitric acid of reagent bottles soon becomes brown.

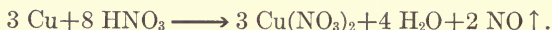
When the vapors of nitric acid are passed through a hot tube they are completely decomposed into nitrogen dioxide, water, and oxygen.

As an acid, nitric acid neutralizes solutions of bases, forming with them *nitrates* and water, just as hydrochloric acid forms chlorides and water.

227. Action of Nitric Acid upon Metals. — The tendency of nitric acid to break up into oxides of nitrogen and free oxygen (*cf.* § 226) determines its general chemical behavior; for nitric acid is not only a strong acid, but a powerful **oxidizing agent**. When, therefore, we compare the action of nitric acid upon

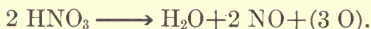
metals with that of hydrochloric and dilute sulphuric acids, we observe a great difference; for while the acids just named generally give up hydrogen when treated with metals, nitric acid rarely does so. Instead of setting hydrogen free, the metal usually reduces some of the nitric acid to nitrogen oxides or, even lower, to *hydroxylamine*, NH_2OH , and to ammonia.

The reaction of **copper** with dilute nitric acid is typical. The products are cupric nitrate, water, and *nitric oxide* (cf. § 237).



The **stages** of the reaction are probably as follows:—

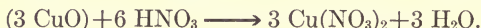
(1) The decomposition of nitric acid according to the general equation:—



(2) Oxidation of copper to cupric oxide:—

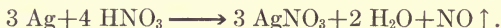


(3) The reaction of cupric oxide and nitric acid (cf. § 162):—

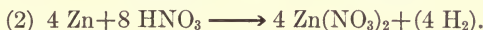
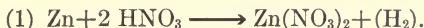


(4) The **complete equation**, given above, is made by combining the partial equations, the intermediate products (in parentheses) being eliminated.

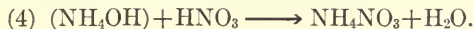
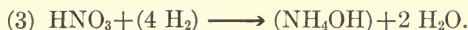
For **silver** and nitric acid the equation is similar, except that the metal is *univalent*,—



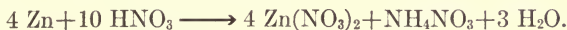
Zinc and dilute nitric acid (5% to 6%) give zinc nitrate, water, and *ammonium nitrate*. In this case *hydrogen* may be an intermediate product. If so, the probable equations are: —



This is equation (1) multiplied by 4.



Hence the *complete equation* is,



The reduction of nitric acid to ammonia can be shown by the addition of a little of the dilute acid to a warm mixture of zinc dust and sodium hydroxide solution (*cf.* § 447).

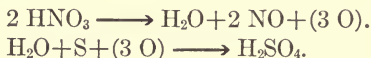
228. Aqua Regia. — Gold and platinum alone of all the more common metals do not react with nitric acid. As was stated under Chlorine (*cf.* § 116), these two metals are soluble in *aqua regia* and in chlorine water.

Aqua regia is made by mixing nitric acid with hydrochloric acid (three volumes of hydrochloric acid to *one* of nitric acid); it is merely a *source of nascent chlorine*.

Aqua regia is used to dissolve many other metals besides gold and platinum.

229. Oxidation by Nitric Acid. — It is not only toward metals that nitric acid acts as an oxidizing

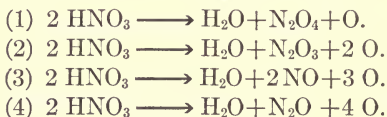
agent. Phosphorus is converted by it into phosphoric acid, and sulphur into sulphuric acid.



Glowing charcoal burns in the acid much as it would in oxygen itself. Organic coloring matters, *e. g.*, indigo solution, are oxidized by nitric acid to colorless bodies.

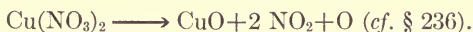
The oxidizing power of nitric acid is much greater if some of the higher oxides of nitrogen are present. Such an acid is **fuming** nitric acid, a red liquid containing much nitrogen dioxide, NO_2 . This acid is used for very rapid oxidation.

It is evident that the oxidizing action of nitric acid is due to its **instability**. One of the products is always *water*; the oxides of nitrogen produced are decomposition products of *nitrogen pentoxide*, the anhydride of nitric acid. The following equations represent *some* of the stages of the decomposition: —

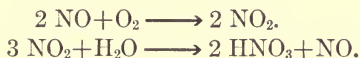


Which of the nitrogen oxides will be formed depends on the concentration of the acid, the temperature, and the reducing agent. Equation (1) represents what occurs when concentrated nitric acid is heated, or treated with metals. Equation (2) is for the action of starch, arsenic trioxide, etc., with acid of specific gravity 1.3. Equation (3) is for copper, silver, etc., and acid of specific gravity 1.2. Equation (4) is for zinc and nitric acid of specific gravity 1.1.

230. Nitrates. — All nitrates, like nitric acid, are unstable, and act as **oxidizing agents** (*cf.* § 25). All but those of sodium, potassium, and ammonium (*cf.* §§ 234 and 238) break up, when heated, essentially like nitric acid (*cf.* § 226), except that the *oxide of the metal* is formed instead of water. Cupric nitrate is an example: —



231. Sources of Nitrates. — When electric discharges pass through air, some *nitric oxide* (NO) is formed. This reacts with water and oxygen, giving *nitric acid*: —



Much nitric acid is probably formed in this way, and gets into the soil (*cf.* § 188). In imitation of this method some nitric acid is now being prepared by the action of powerful electric arcs upon air.

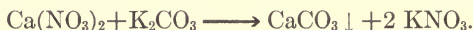
This process of *synthesizing* nitric acid is very important, in view of the fact that nitrates are used extensively as *fertilizers* (*cf.* § 358), and that the natural supply is very limited. The most extensive nitrate deposits are those of *sodium nitrate* (Chili saltpeter) found in the Atacama Desert, in Chili. “Nitrate beds” were probably formed by the action of **oxidizing bacteria** (*cf.* § 25) *upon nitrogenous organic substances*, in the presence of alkali. In certain parts of Europe farmers cultivate nitrates by adding the proper bacteria to a mixture of alkali and nitrogenous matter.

Potassium nitrate is made by mixing *hot, concentrated* solutions of sodium nitrate and potassium chloride.



The sodium chloride is filtered off while the mixture is hot. When the filtrate is cooled, almost pure potassium nitrate crystallizes out.

Potassium nitrate was formerly obtained almost entirely from Asia. In the neighborhood of cities a deposit of calcium nitrate appears on the ground. This is collected, and the solution is treated with wood ashes, which contain potassium carbonate (*cf.* § 422).



232. Uses of Nitric Acid and the Nitrates. — Nitric acid is used in making sulphuric acid by the “Chamber Process” (*cf.* § 262), and in making nitrobenzene, “nitroglycerine,” collodion, gun-cotton, celluloid, etc.

Glyceryl nitrate (wrongly called nitroglycerine) is made by the action of a mixture of concentrated nitric and sulphuric acids at a low temperature upon glycerine. It is a thick, greenish liquid of a very unstable nature, and very explosive. It is usually mixed with a porous earth, and appears in the market chiefly as *dynamite*.

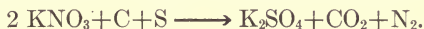
Gun cotton and *collodion* are nitrates of cellulose (*cf.* § 548). They are made by the action of a mixture of nitric and sulphuric acids upon cotton. Gun cotton is used as an explosive. It is not soluble in a mixture of alcohol and ether, while **collodion** is. When the solvents evaporate, the collodion is left as a tough, transparent layer. It is used to make photographic films, and

to protect wounds from the air. **Celluloid** is a mixture of gun cotton and camphor.

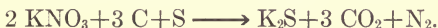
Nitrobenzene is made from benzene, C_6H_6 , and the nitric-sulphuric acid mixture. When nitrobenzene is reduced by nascent hydrogen, it gives *aniline*, the starting material in the manufacture of the aniline dyes.

The *nitrates* are used in the manufacture of gunpowder and various explosives, in the preservation of meats, e. g., "corned beef," and as fertilizers. **Gunpowder** is a physical mixture of potassium nitrate, sulphur, and charcoal, in various proportions (*cf.* § 26). The relative amounts of the constituents vary, according to the purpose for which the powder is to be used. When gunpowder is ignited, it forms gases that occupy several hundred times as much space as the original powder.

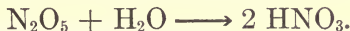
The reactions taking place in the explosion of one kind of gunpowder are probably represented by the equation, —



Another equation is: —



233. Nitrogen Pentoxide. — Nitrogen pentoxide ("penta" = five) is of theoretical importance because it is the *anhydride* of nitric acid, *i. e.*, it is nitric acid *minus* water. The relation of nitrogen pentoxide to nitric acid is evident from the equation,



Nitrogen pentoxide is a white, crystalline solid, made by the distillation of anhydrous nitric acid with phosphorus pentoxide.

234. Nitrous Acid. — Nitrous acid is probably contained in a solution of nitrogen trioxide in water;

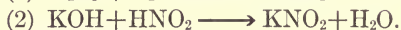
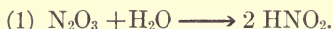
nitrogen trioxide is, therefore, called *nitrous anhydride*, just as nitrogen pentoxide is *nitric anhydride*. This relation is shown by the equation, —



The meaning of the ending *ous* as applied to nitrous acid has already been given (cf. § 168).

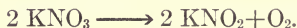
Nitrous acid itself has not been made; but its *salts* (called *nitrites* to distinguish them from the salts of nitric acid) are formed when a solution of nitrogen trioxide is neutralized by bases.

Thus, potassium hydroxide and a solution of nitrogen trioxide give potassium nitrite and water, as is shown by the equations, —



A second way in which nitrites are formed is by the abstraction of oxygen from *nitrates*.

Thus, potassium nitrate loses one-third of its oxygen when heated to a high temperature. The equation is, —



The temperature required is much lower if the nitrate is mixed with lead when heated; for the lead unites with the liberated oxygen to form lead oxide, PbO.

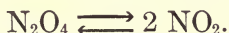
235. Nitrogen Trioxide (N_2O_3). — As was stated in § 234, nitrogen trioxide is the anhydride of nitrous

acid. It may be made by the action of nitric acid of specific gravity 1.3 upon *arsenic trioxide* or upon *starch*.

The brown fumes *called* the trioxide may be condensed by a freezing mixture to a blue liquid, which is the *real* trioxide. When, however, this liquid is distilled, the vapors are not nitrogen *trioxide*, but a mixture of the *dioxide* (NO_2) with *nitric oxide*.

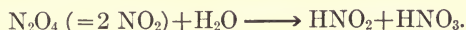
* 236. **Nitrogen Dioxide and Nitrogen Tetroxide** (NO_2 and N_2O_4). — *Nitrogen dioxide* lies between nitrogen trioxide and nitrogen pentoxide as regards the proportion of oxygen it contains. Below 22°C . it is a liquid; but it is usually known in the form of its vapor.

Nitrogen tetroxide ("tetra" = four) exists at low temperatures, but it *dissociates* readily, to some extent even at 0°C ., into nitrogen dioxide. Dissociation increases as the temperature rises: —



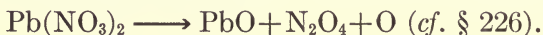
The *degree* of the dissociation is shown by the darkening of the color, nitrogen tetroxide being colorless, but nitrogen dioxide brown.

When nitrogen tetroxide is dissolved in much cold water, the solution contains a mixture of nitrous and nitric acids; hence nitrogen tetroxide is the anhydride of both of these acids. The equation showing this fact is, —



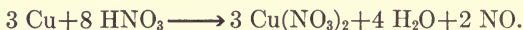
* The names used are in accordance with the latest nomenclature.

Nitrogen tetroxide is formed when most nitrates (*cf.* § 230) are heated. The vapors may be condensed by passing them through a U-tube surrounded by a freezing mixture. The decomposition of lead nitrate corresponds exactly with that of nitric acid, as is shown by the equation, —



237. Nitric Oxide (NO). — Two other oxides of nitrogen are known, *viz.*, *nitric oxide* and *nitrous oxide*; both are colorless gases at the ordinary temperature and pressure.

Nitric oxide is produced when nitric acid of specific gravity 1.2 is allowed to react with copper. The equation has already been given (*cf.* § 227). It is, —



Nitric oxide is slightly heavier than air. One liter of it weighs, under standard conditions, 1.34 grams. The gas is only slightly soluble in water.

When nitric oxide is passed into a solution of ferrous sulphate, FeSO_4 , large quantities of the gas are absorbed, a brown compound of ferrous sulphate and nitric oxide being formed. When the solution containing this compound is heated, pure nitric oxide escapes.

Nitric oxide becomes brown when it comes into contact with air or oxygen, owing to the formation of *nitrogen dioxide*.

One volume of nitric oxide consists of one-half a volume of nitrogen and one-half a volume of oxygen.

The amount of the nitrogen may be shown by heating a piece of metallic sodium in a measured volume of the gas over mercury (see Fig. 52). The sodium combines with the oxygen of the nitric oxide, leaving the nitrogen. *The volume of the nitrogen should be just half that of the nitric oxide taken.*

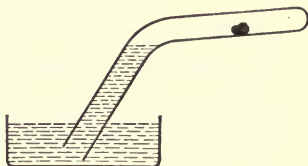


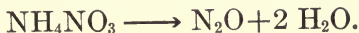
FIG. 52.

Nitric oxide supports the combustion of phosphorus and of magnesium, as well as of sodium.

238. Nitrous Oxide (N_2O). — Nitrous oxide is commonly made by heating ammonium nitrate (NH_4NO_3) to $170^\circ C.$, or, better, by heating a mixture of sodium nitrate and ammonium sulphate to a slightly higher temperature.

The formation of nitrous oxide is the result of several reactions. At first the ammonium nitrate probably dissociates into ammonia and nitric acid just as ammonium chloride gives ammonia and hydrochloric acid. The ammonia and nitric acid do not, however, recombine when cool, because the nitric acid *oxidizes* the hydrogen of the ammonia to water.

The *final* equation for the decomposition of ammonium nitrate is, —



Compare with this the equation for the decomposition of ammonium nitrite (§ 187). Note that *all* of the hydrogen is oxidized to *water* in each case, and that it is the oxygen in excess of that required to oxidize hydrogen that causes the formation of nitrous oxide when ammonium nitrate is decomposed.

Nitrous oxide is the only gas besides oxygen that will re-ignite a glowing splinter.

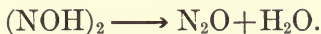
The *volumetric composition* of nitrous oxide may be determined in the same way as that of nitric oxide, viz., *by taking out the oxygen by means of sodium*. There is, however, a great difference in results; for while one volume of nitric oxide contains one-half a volume of nitrogen and one-half a volume of oxygen, one volume of nitrous oxide contains one volume of nitrogen and one-half a volume of oxygen.

Nitrous oxide may be condensed to the liquid form; as such it is a commercial article. When the pressure under which the gas is kept is removed, some of the liquid vaporizes, producing the "laughing gas" which dentists use to produce insensibility to pain.

Nitrous oxide is easily soluble; 1 volume of water at 0° C. absorbs 1.3 volumes of the gas. One liter at standard conditions weighs 1.97 grams.

239. Hyponitrous Acid (NOH)₂.—Hyponitrites, *i. e.*, salts of hyponitrous acid, have been known for some time, but the acid itself has only recently been isolated. A solution of hyponitrous acid decomposes

readily, giving nitrous oxide, according to the equation, —



Nitrous oxide may thus be looked upon as *in some sense* the *anhydride* of hyponitrous acid; but the union of nitrous oxide and water to form the acid does not take place.

240. Exercises.

1. How many grams of nitric acid can be made, theoretically, from 1 kg. sodium nitrate with sulphuric acid?
2. What will be the volume of 28.4 grams of commercial nitric acid?
3. How much sulphuric acid (calculated as 100% H_2SO_4) will be needed to give 1,260 grams of nitric acid with potassium nitrate, if potassium hydrogen sulphate is formed?
4. Calculate the percentage composition of nitric acid?
5. How much potassium hydroxide is required to neutralize exactly a solution containing 42 grams nitric acid?
6. How could you separate a mixture of silver and gold chemically?
7. How many grams nitrogen tetroxide could be made from 450 grams lead nitrate? How much oxygen?
8. How many grams nitric oxide can be made, theoretically, from 100 grams nitric acid with copper? How much copper is needed? How much cupric nitrate is formed?
9. How many liters of nitrous oxide at 0°C . and 760 mm. can be made from 240 grams ammonium nitrate? How many at 20°C . and 720 mm.?
10. How would you distinguish between nitrous oxide and oxygen?
11. How many cubic centimeters of each of its constituents combine to form 100 c.c. nitric oxide? To form 100 c.c. of nitrous oxide?

12. Name three different classes of nitrates, basing the difference upon the way in which the members of each class decompose when heated.

13. Change the last equation in § 236 to a *molecular equation*. If you were to collect a given volume of the gases evolved in this reaction, what per cent, by volume, would be oxygen? Suggest how you could remove the nitrogen tetroxide, and leave the oxygen.

CHAPTER XX.

EQUILIBRIUM AND MASS ACTION.

241. Equilibrium. — In Physics we consider a body that is at rest as acted upon by *opposing* forces. Thus, a weight held in the hand is acted upon by *gravity*, which is pulling it toward the earth, and by the muscular force of the arm and hand, which opposes gravity. Neither force ceases to act, but the weight does not move, because the two forces are “**in equilibrium**,” or “*balance*” *each other*. This idea of equilibrium applies to all physical and chemical changes. In physical changes, such as *solution* and *change of physical state*, we call it **physical equilibrium**; as applied to *chemical* reactions, it is called **chemical equilibrium**.

242. Physical Equilibrium. *a. Between Solute and Solution.* — When a solute is brought in contact with a solvent, the solute expands to fill the solvent much as a gas expands into a vacuum. As soon as some solute has dissolved, dissolved particles begin to return to the undissolved state. These two opposing operations go on until they are equal, that is, until as many molecules *separate* from solution in a given time as *dissolve* in the same time. The

condition in the solution is then one of *physical equilibrium* between dissolved and undissolved solute. It is expressed by the *equilibrium equation*.



The double arrow is read "*is in equilibrium with.*" When this condition of equilibrium exists the solution is **saturated** (cf. § 84). Solution and separation from solution continue, for the energy of the molecules remains, but if the temperature and pressure remain constant, the solution becomes neither more concentrated nor more dilute. *If we change the conditions slightly, however, equilibrium is set up for the new conditions.* Thus if we have undissolved potassium nitrate in equilibrium with its saturated solution at 20° C., and raise the temperature to 25° C., potassium nitrate dissolves until there is equilibrium at the higher temperature.

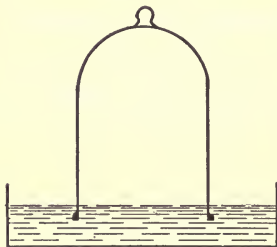
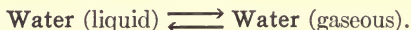


Fig. 53.

(b) *Between a Liquid and its Vapor.* If a vessel of air be inverted over water (cf. Fig. 53), **two physical equilibria** are soon set up:—

(1) The molecules of water leave the water surface (as steam) and enter the air layer; at the same time molecules of steam return to the water. When the two actions are equal, there is equilibrium:—



The air is then "saturated" with water vapor.

(2) The molecules of air, *i. e.*, of its constituents, *enter* the water, and dissolved air *leaves* the water, until the two actions are equal.

Air (undissolved) $\rightleftharpoons$ Air (dissolved).

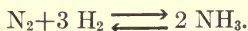
The water is then “saturated” with air. In case (1), as in the case of the potassium nitrate, a change in conditions alters the point at which equilibrium is reached. If the temperature is raised, more water will change to steam to produce saturation. If the air layer be in motion, as when water stands in an open dish, equilibrium is never reached; hence, the water “*evaporates*.”

243. Chemical Equilibrium. — Just as we may have two opposite physical changes “balancing” each other, so there may be two chemical reactions which, if carried to completion, would give exactly opposite results. Two reactions so related are the following (*cf.* § 213):

(1) Nitrogen and hydrogen unite, under the influence of the electric discharge, to give ammonia.

(2) Ammonia is decomposed, under the same conditions, giving nitrogen and hydrogen.

Each of the reactions is **reversible**, and both may be represented by the equilibrium equation, —



The reason for the reversibility is that all the substances concerned are gaseous, and, therefore, re-

main subject to the action of the electric discharge. The conditions are, thus, similar to those existing when *physical* equilibrium results: *nothing is removed from the sphere of action*. If any one of the three substances is removed, the reaction will go to completion.

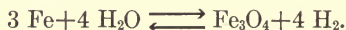
The equilibrium between steam, hydrogen, and oxygen ("dissociation of steam") at high temperatures is another case of the same sort (*cf.* § 73).

For a third case we have the two reversible reactions given under "Hydrogen" (*cf.* §§ 56 and 57):—

(1) When steam is passed over heated iron the products are magnetic iron oxide and hydrogen.

(2) When hydrogen is passed over the heated iron oxide, the products are steam and iron.

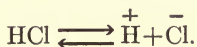
The equation for both is the equilibrium equation, —



If steam acted upon iron, or hydrogen upon iron oxide, *in a closed tube*, this condition of equilibrium would be reached. But when steam is passed over iron, the hydrogen produced is carried away by the steam, and the reaction, as read from left to right, is a **complete** one. In the same way, the reverse action becomes complete if the steam formed is removed by the hydrogen.

244. Ionic Equilibrium. — Under "ionization" we learned that for ordinary concentrations ionization is incomplete. Thus *normal* hydrochloric acid (*cf.* § 178) is 78.4% dissociated at 18° C. Why is the dissociation incomplete? The answer is that while the solvent permits (or causes) the dissociation, the

oppositely charged ions unite, in part, to form the molecular ionogen.

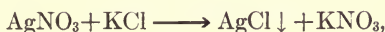


Here, again, equilibrium is reached. Raising the temperature and diluting the solution increase the ionization; lowering the temperature and concentrating the solution cause the ions to recombine.

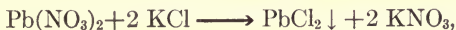
245. Chemical Equilibrium in Solution. — All reactions, in solution, of the type,



are **reversible**, unless either AD or BC is insoluble. Thus, the reaction represented by the equation,

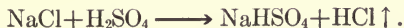


is practically complete, because of the slight solubility of silver chloride (*cf.* § 179), but the reaction,



is much less complete, because lead chloride is more soluble than silver chloride (*cf.* **Appendix**, viii).

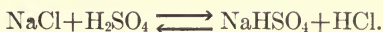
The reactions for the preparation of *nitric acid* and *hydrogen chloride* are true reversible reactions (*cf.* § 225), but they become practically complete because the acids are removed in gaseous form. Thus, —



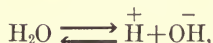
The reversibility of this reaction may be shown by mixing concentrated solutions of sodium hydrogen sulphate and hydrochloric acid. Sodium chloride is precipitated.



In more dilute solutions, all the substances are soluble, and there is **equilibrium**: —



In all the cases considered, double decomposition reactions become complete because one of the products is removed in an insoluble form. In **neutralization** this is not the case: the completeness of the reaction depends, rather, on the fact that water is only *very slightly dissociated*. Yet, slight as is the ionization represented by the equation,

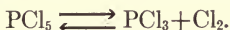


it is sufficient to produce **hydrolysis** (*cf.* § 184) of salts formed from any but the strong acids and bases.

246. Mass Action. — The combination of particles (molecules or ions), whether in gaseous form or in solution, is influenced by the *frequency* with which the particles *meet*. If, therefore, we wish to stop or to diminish the dissociation of a substance AB, we see to it that an *excess* of one of the particles produced by the dissociation, *e. g.*, A, is present. By thus increasing the **active mass** of A, we diminish the possibility that B can exist uncombined with A.

The action of an **excess** of one of the substances (or ions) produced in a reversible reaction is called **Mass Action**.

To illustrate: the molecular weight of *phosphorus pentachloride*, PCl_5 , as determined by vapor density methods, is too *low*, owing to the dissociation of some of the molecules into *phosphorus trichloride* and *chlorine*.

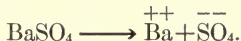


The dissociation can be prevented if the vapor density determination is carried out in an atmosphere of phosphorus trichloride; because the chlorine molecules then meet molecules of phosphorus trichloride so frequently that practically no chlorine molecules remain free.

Similar effects occur in solution. Thus, if we wish to precipitate the sulphuric acid, *i. e.*, the SO_4 ions, contained in a solution, we use *barium chloride* solution. If we use exactly the *theoretical* amount of barium chloride, however, much barium sulphate remains in solution (as Ba and SO_4 ions). The reaction is only partly represented by the equation, —



for the *reverse* operation also goes on.



Whatever will cause the SO_4 ions to meet more Ba ions in a given time will increase the precipitation of the SO_4 ions as barium sulphate. We obtain this result by adding a large *excess* of barium chloride solution.

247. Exercises.

1. How does the amount of steam necessary to “saturate” a given volume of air (*cf.* Fig. 53) compare with the amount that

would evaporate into this space if air were not present; that is, if the space were a "vacuum"?

2. Write the equation showing the equilibrium between water at 0°C . and some ice floating in it, if the room is also at 0°C . What change would occur if the temperature of the room were raised slightly?

3. Write the equation for the equilibrium between salt in contact with a saturated salt solution. What result would follow if water were added? If concentrated hydrochloric acid were added? Why?

4. To precipitate all the *manganese* of manganous sulphate solution as the sulphide, MnS (*cf.* § 256), we use an **excess** of sodium sulphide. Why?

5. Write the equation for the equilibrium between *ammonium hydroxide* and its ions. For the equilibrium between *ammonium chloride* and its ions. If a *concentrated* solution of ammonium chloride were added to ammonium hydroxide, would the mixture be as strong a base as the ammonium hydroxide alone? Why?

CHAPTER XXI.

SULPHUR AND ITS COMPOUNDS.

248. Occurrence and Preparation of Sulphur. —

Sulphur occurs in nature in both a free and a combined form. In the free condition it is obtained chiefly from Sicily, Mexico, and, to some extent, from Louisiana. Natural sulphur is usually found mixed with much earthy material, from which it must be separated to prepare it for the market.

The *first* operation in the purification of sulphur usually consists in heating the natural product; the sulphur melts and flows away, leaving the infusible impurities behind.

In the *second* operation the partially purified sulphur is distilled from large iron retorts (see Fig. 54), and is thus separated from less volatile impurities.

The melted sulphur in the reservoir *A* is allowed to flow from time to time into the retort *B*, in which the sulphur is vaporized.

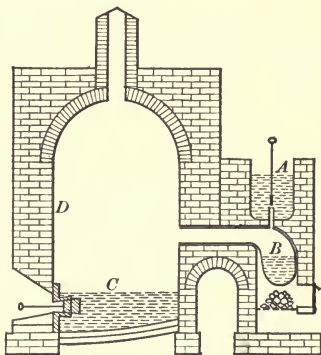


FIG. 54.

The sulphur vapor which passes into the condenser collects either in the liquid state, at the bottom (*C*) of the condenser, or in a solid state upon the cold walls (*D*). The *liquid* sulphur is run into molds to crystallize, thus producing the "roll-sulphur," or "brimstone" of commerce; the sulphur which solidifies upon the walls appears in the form of fine *meal* and is called "flowers" (more correctly, "*flour*") of sulphur.

249. Physical Properties; Allotropism. — Sulphur, like many other elements, exists in several different physical forms; consequently, in giving the properties of sulphur we must specify the *kind* of sulphur to which we are referring. The several varieties of sulphur may be grouped into three classes: —

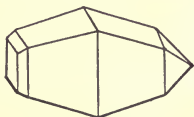


FIG. 55.

(1) **Ordinary**, or *rhombic*, sulphur (cf. Fig. 55 and **Appendix**, xi). This is the natural form. All other forms revert

to it at the ordinary temperature. It is yellow, odorless, tasteless, melts at 114.5°C ., has a specific gravity of 2.06, and is very soluble in carbon disulphide — 46 g. in 100 g. of CS_2 at the ordinary temperature. In water it is insoluble. *Roll sulphur* is rhombic; so are the crystals that separate from carbon disulphide solution.

(2) **Prismatic**, or *monoclinic*, sulphur (Fig. 56). This is formed by **slow cooling** of melted sulphur. As soon as a crust forms, it is broken, and the liquid sulphur is poured off. The crystals are long, almost colorless needles, that melt at 119°



FIG. 56.

C ., and dissolve in carbon disulphide. Their specific gravity is 1.96. If kept below 96°C ., they change, in a few days, to the

rhombic form, **with evolution of heat**. On the other hand, *rhombic sulphur changes to prismatic* above 96° C.

(3) **Amorphous**, *i. e.*, *non-crystalline*, sulphur. Ordinary sulphur behaves peculiarly when heated. At 114.5° C. it becomes a yellow liquid. Above 160° C. it is dark and viscous, and at 230° it can hardly be poured. Above 300° C. it is limpid again, and at 445° it boils, giving a light-brown vapor. If it is allowed to cool slowly, these changes are repeated, in the reverse order, and ordinary sulphur is *finally* obtained. If, however, boiling sulphur is *chilled* suddenly, as by pouring it into cold water, the product is an elastic, non-crystallized substance. After several days this becomes hard, and consists partly of rhombic sulphur, which is soluble in CS_2 , and partly of an amorphous variety, which is **insoluble** in CS_2 . Amorphous sulphur is the hardened form of the dark, viscous liquid. Because of the sudden cooling, it was not given time to change into the ordinary form. When it is kept below 96° , it changes slowly into rhombic sulphur **with evolution of heat**. At the ordinary temperature the change may take years.

"Flowers of sulphur" have a nucleus of rhombic crystals and an amorphous covering.

Allotropism. — The existence of an element in several physical forms is called **allotropism**, and the different varieties are called *allotropic forms* of the element. Allotropism may be due to *different arrangements* of the atoms in the molecule, to *different numbers* of atoms in the molecule, or to other causes. In the change of one form into another, an *energy-change* is usually observed (*cf.* § 312).

250. Chemical Properties. — Sulphur unites directly with many elements, especially with metals. Thus, when a mixture of powdered iron and sulphur is heated, or moistened with water, or strongly compressed, it unites chemically, forming ferrous

sulphide, FeS . Similarly, copper foil burns in sulphur vapor, giving cuprous sulphide. Mercury combines with sulphur when the two are simply *trituated*, i. e., rubbed together in a mortar.

There are many *common* illustrations of the action of sulphur upon metals. Thus, silver egg-spoons are blackened by the sulphur contained in eggs; and silver coins which have been carried about in the pockets are colored by the sulphur of the perspiration.

The illuminating gas of many cities contains sulphur compounds; this fact accounts for the tarnishing of articles of brass, copper, lead, silver, etc., in houses in which such gas is used.

At about 260°C . sulphur begins to unite with the oxygen of the air. If sulphur at a temperature slightly below 260°C . is examined in the dark it will be found to **phosphoresce**, i. e., *glow*.

In burning, sulphur produces sulphur *dioxide*, SO_2 . This is an invisible gas having the characteristic odor of burning sulphur.

251. Uses of Sulphur. — Sulphur is used in the preparation of many important substances. Thus, *rubber goods* and *vulcanite* are made by heating together caoutchouc and sulphur; *match tips*, especially the older forms, contain sulphur as an ingredient; *gunpowder*, as previously stated, is a mixture of charcoal, sulphur, and niter; and sulphur dioxide, which is used for *bleaching* and as a *germicide*, is made by burning sulphur in air.

Finally, sulphur is used in the preparation of *sulphuric acid*, which is possibly the most important substance manufactured.

252. Compounds of Sulphur. — Sulphur is a constituent of many important compounds; for the *sulphides*, next to the oxides, are the most common ores of the metals. Among the natural sulphides are *iron pyrites* (FeS_2), *galena* (PbS), and *hydrogen sulphide* (H_2S). The latter is a gas under ordinary conditions.

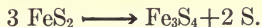
The two important *oxides* of sulphur are *sulphur dioxide* and *sulphur trioxide*.

With hydrogen and oxygen sulphur forms *sulphuric acid* and other acids, and with metals and oxygen, *sulphates*, *sulphites*, *thiosulphates*, etc.

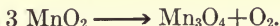
The most important *natural* sulphate is *gypsum*, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$. Natural barium sulphate, BaSO_4 , is called "*heavy spar*." Both are important minerals.

Iron pyrites, FeS_2 , is a source of both sulphur and sulphur dioxide. When it is *roasted*, i. e., heated in a current of air, its sulphur is oxidized to sulphur dioxide, SO_2 , but if the iron pyrites is heated *without access of air* it breaks down into a compound of iron and sulphur containing only two-thirds of the sulphur of the original pyrites. The excess of sulphur is liberated.

The equation representing this reaction is, —



The reaction is like that which takes place when manganese dioxide is heated (cf. § 22), and which is indicated by the equation,

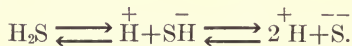


253. Hydrogen Sulphide. — Hydrogen sulphide is a colorless gas formed by the decomposition of organic substances containing sulphur. It has the odor of rotten eggs. So-called "sulphur" waters contain it. Its specific gravity is 1.18 (air = 1). Hydrogen sulphide is usually prepared by the action of dilute hydrochloric or sulphuric acid upon ferrous sulphide.



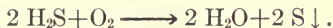
Hydrogen sulphide is decomposed by heat into its elements. A **jet** of the gas burns completely to water and sulphur dioxide, but when the supply of air is limited, as in the burning of a bottle of the gas, the hydrogen burns, but some of the sulphur does not.

Under standard conditions one volume of water absorbs 3 volumes of the gas. The solution is a weak acid — **hydrosulphuric acid**. Its ionization is expressed by the double equilibrium equation, —

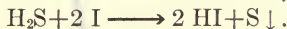
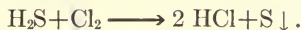


In writing equations containing H_2S , we consider its ions to be $2 \overset{+}{\text{H}} + \overset{--}{\text{S}}$.

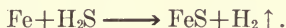
The aqueous solution is easily decomposed, especially in the light and when warm, by the oxygen of the air; hence it soon loses its odor, and deposits **sulphur**.



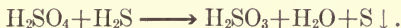
Chlorine and iodine react with hydrogen sulphide solution in a similar way: —



The gas and its solution react with most metals, giving sulphides and hydrogen: —



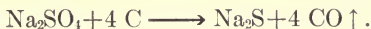
Hydrogen sulphide is, as we might expect, a **reducing agent**. Thus, it reduces concentrated *sulphuric* acid to *sulphurous* acid (cf. § 265): —



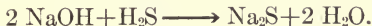
254. Sulphides. — The *salts* of hydrosulphuric acid are the sulphides. They are formed in several ways:

- (1) By the union of metals with sulphur.
- (2) By the action of metals with hydrogen sulphide.
- (3) By the reduction of a sulphate or sulphite.
- (4) By the reaction between a base and hydrosulphuric acid.
- (5) By the reaction between hydrogen sulphide, or some other soluble sulphide, and soluble salts of some metals.

An illustration of the *third* method is the reduction of sodium *sulphate*, when heated with charcoal, to sodium *sulphide*: —



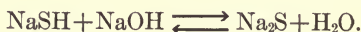
An illustration of the *fourth* method is the absorption of hydrogen sulphide by sodium hydroxide solution: —



Hydrosulphides.—If we pass hydrogen sulphide into sodium hydroxide solution as long as it is absorbed, we get **sodium hydrosulphide**, NaSH:—

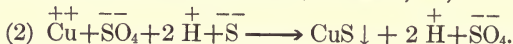
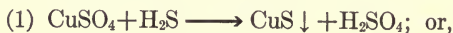


This forms a solution **neutral** to litmus. If, now, we add to the NaSH as much NaOH as was used originally, we obtain an **alkaline** solution containing Na_2S *in equilibrium with* NaSH and NaOH:—

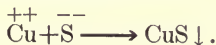


Evaporation of the solution gives crystalline Na_2S . Ammonium sulphide, $(\text{NH}_4)_2\text{S}$, is prepared (in solution) in a similar way.

255. Precipitation of Sulphides.—The **fifth** method of forming a sulphide, *i. e.*, by the addition of a soluble sulphide to the salt of a metal, will succeed only if the sulphide desired is **insoluble** in the solvent used. Thus, hydrogen sulphide reacts with cupric sulphate solution to give **cupric sulphide** (a black precipitate) and sulphuric acid:—



Since CuS is *very insoluble*, both in water and in dilute acids, all the ionic copper of the solution may be removed by H_2S , *i. e.*, by $\overset{--}{\text{S}}$:—

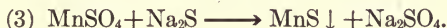


But no result follows when H_2S is added to *sodium sulphate*, because all of the products are soluble:—

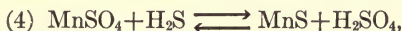


Another fact must be considered in this connection: many sulphides that are not precipitated by hydrogen sulphide are precipitated by a *metal sulphide*, *e. g.*, Na_2S .

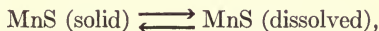
This is the case with *manganous sulphide*, MnS :—



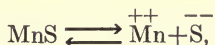
The equilibrium reaction represented by the equation, —



is forced *backward*, giving hydrogen sulphide, rather than *forward*, to give manganous sulphide, owing to the action of the sulphuric acid upon the manganous sulphide. *No MnS is precipitated.* We ought to expect this, since H_2S is commonly prepared from a sulphide (FeS) by the action of an acid (*cf.* § 253). The difference between the reactions of equations (3) and (4) is due to the fact that MnS , in spite of its **apparent** insolubility [equation (3)], is still *appreciably soluble in water*. That is to say, the change expressed by the physical equilibrium equation (*cf.* § 242), —



goes *forward* to an appreciable extent. The dissolved MnS is *ionized*, —



and the sulphuric acid, *i. e.*, $\overset{+}{\text{H}}$, reacts with $\overset{--}{\text{S}}$, giving H_2S . Hence H_2S escapes from the solution as rapidly as it is added. The Na_2S [equation (3)] gives $\overset{--}{\text{S}}$, but not $\overset{+}{\text{H}}$, hence the reverse action

is not appreciable, and *MnS* is *precipitated*. The solubility of *CuS* [equations (1) and (2)] is so small that the reverse action due to the H_2SO_4 is insignificant.

The sulphides of the metals are thus divided into **three groups**:

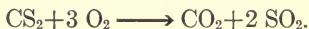
(1) The **soluble sulphides**, such as Na_2S , BaS , etc. These are *not precipitated*, either by H_2S or by a metal sulphide.

(2) The **very insoluble** sulphides, such as Ag_2S , PbS , CuS , and As_2S_3 . These are precipitated by H_2S , *even if a dilute acid is present*.

(3) The **moderately insoluble** sulphides, such as FeS , MnS , ZnS , etc. These are not precipitated by H_2S , or only slightly (not at all if acid is added), but *are* precipitated by a metal sulphide, such as Na_2S and $(\text{NH}_4)_2\text{S}$.

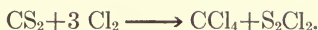
These facts form the basis of that branch of Chemistry called **qualitative analysis**, for they enable us to classify all the common metals into three groups.

256. Carbon Disulphide (CS_2). — Carbon disulphide is formed by the direct union of carbon and sulphur. The old method was to pass sulphur vapor over hot charcoal ; in the modern method an electric furnace is used to bring about the reaction. Pure carbon disulphide is colorless, and has an ethereal odor; but as obtained commercially it is often yellow, and has a disagreeable smell. The liquid boils at 47°C ., and has a specific gravity of 1.27. It is very *inflammable*.

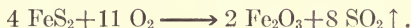


The chief use of carbon disulphide is as a **solvent** for sulphur, caoutchouc, phosphorus, iodine, resins and waxes. It is also an **insecticide**. *Carbon tetrachloride*, CCl_4 (*cf.* § 533), used as a non-

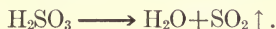
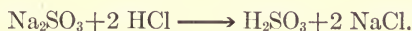
inflammable cleaning agent for fabrics, is made from carbon disulphide: —



257. Sulphur Dioxide. — Sulphur dioxide is the gas of well-known odor produced by burning sulphur in air or oxygen. Commercially it is usually formed by *roasting* a sulphide, *e. g.*, iron pyrites (*cf.* § 252).



Sulphur dioxide is formed by the spontaneous decomposition of *sulphurous acid*, H_2SO_3 . When, therefore, this acid is formed in a double decomposition, as when a sulphite is treated with a strong acid, sulphur dioxide results.



The **common laboratory method** is to heat concentrated sulphuric acid with copper.



The stages of the reaction are given in § 265. Sulphur dioxide is colorless, and 2.2 times as heavy as air. It is very soluble in water — 80 c.c. in 1 c.c. water at 0° C. The gas is expelled when the solution is heated.

Sulphur dioxide may be obtained in liquid form (Fig. 57) by passing it through a condensing tube (conveniently in U form) surrounded by a freezing mixture of ice and salt. The resulting liquid is colorless; it boils at -8°C . The evaporation of liquid sulphur dioxide absorbs much heat; hence this substance is often used as a refrigerating agent.

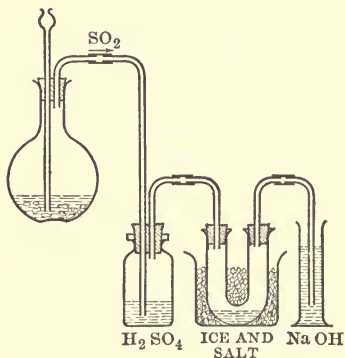
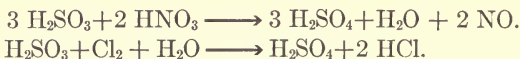


FIG. 57.

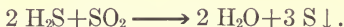
258. Chemical Properties of Sulphur Dioxide.

— Most of the chemical properties of sulphur dioxide are those of its solution, which contains *sulphurous acid* (§ 259).

This is oxidized *slowly* by the air to sulphuric acid. With oxidizing agents the change is rapid. With nitric acid and with chlorine water the equations are: —



Solutions of potassium chromate, bichromate, permanganate, etc., are all *reduced* by sulphur dioxide. Sulphur dioxide *oxidizes* hydrogen sulphide: —



Natural deposits of sulphur may be formed in this way, as both gases are evolved in volcanic action.

The chief use of sulphur dioxide, aside from its being the source of sulphuric acid, is as a bleaching

agent of silks, woollens, straws, laces, etc., which would be injured by chlorine (*cf.* § 122).

The sulphur dioxide probably unites with the coloring matter of these fabrics, forming colorless compounds. The bleaching effect disappears after a time, however; hence fabrics bleached by sulphur "yellow" with age. Dilute sulphuric acid, also, restores the color of many articles that have been bleached by sulphur dioxide; it probably breaks up the colorless compounds that were formed.

Sulphur dioxide is used also as a disinfectant.

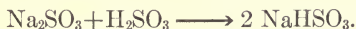
259. Sulphurous Acid. — A solution of sulphur dioxide in water has the properties of a weak acid, and is called sulphurous acid, H_2SO_3 . Sulphur dioxide is, therefore, *sulphurous anhydride*. The free acid has not been isolated (*cf.* § 211).

When sulphurous acid is neutralized by the solution of a base, and the solution is evaporated, a *sulphite* is obtained. The same result follows when sulphur dioxide gas is passed into the solution of an alkali.

As in the case of sulphuric acid, two sets of salts exist. Thus, if an exactly sufficient amount of sulphur dioxide is used with sodium hydroxide, the product is sodium sulphite, Na_2SO_3 . The equation is, —

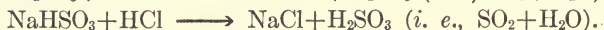
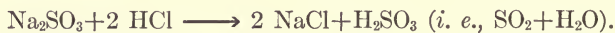


If, however, sulphur dioxide is passed into sodium hydroxide solution until no more gas is absorbed, the solution contains *sodium hydrogen sulphite*, NaHSO_3 . The equation is, —



Similar reactions take place with other bases.

Both normal and acid sulphites are decomposed by dilute sulphuric acid and by hydrochloric acid, giving sulphur dioxide.



By this reaction a *sulphite* may readily be distinguished from a *sulphate*.

Sulphites, like sulphurous acid, oxidize readily in the air.

260. Sulphur Trioxide.—Sulphur trioxide is a colorless liquid above 15°C ., its melting point. Below this it is a white, crystalline solid. The liquid boils at 46° , and is changed by a trace of water to a compact mass of fibrous crystals—the form in which the substance is usually known. In the air, sulphur trioxide gives off dense, choking fumes. It reacts with water, producing a hissing noise and much heat. Sulphur trioxide is **sulphuric anhydride** (*cf.* § 161):—



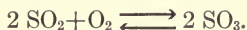
It also combines with the oxides of metals:—



Concentrated sulphuric acid combines with sulphur trioxide, giving **pyrosulphuric acid**, $\text{H}_2\text{S}_2\text{O}_7$. This is also called **fuming sulphuric**, and **disulphuric acid**.

Preparation.—Sulphur trioxide is produced by the oxidation of sulphur dioxide. A small amount is formed when sulphur

burns in air or oxygen. The union of sulphur dioxide and oxygen is incomplete, when the two are heated together, because the **reverse action** takes place: —



When a catalyzer, such as *platinized asbestos*, is used, the combination is made almost complete. The tube containing the

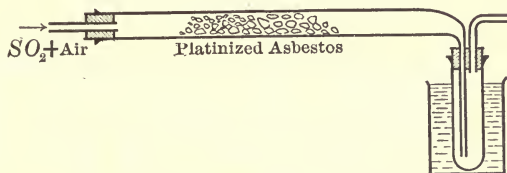


FIG. 58.

catalyzer (Fig. 58) is heated to about 360°C. , and the dry gases are passed through it. The sulphur trioxide may be collected in a cooled receiver, or it may be absorbed by concentrated sulphuric acid. Platinized asbestos is made by soaking fibrous asbestos in chlorplatinic acid, and then decomposing the platinum compound by heat (*cf.* § 517). Other catalyzers, such as vanadium oxide and ferric oxide, are sometimes used.

261. Contact Process for Sulphuric Acid. — The “Contact process” is the more modern of the two common methods of making sulphuric acid. It consists, essentially, in **making sulphur trioxide** (§ 260), and then **treating it with water**. The older process is called the “English,” or “Chamber” process. This consists in *oxidizing sulphur dioxide in the presence of water* (*cf.* § 262).

The **apparatus** used in the contact process is shown in outline in Fig. 59. *A* is the "blower," which furnishes air to the "burner" (*B*), and to the gas "mixer" and "heater" (*H*). In *B* the sulphur compound (commonly, iron pyrites) is oxidized to *sulphur dioxide*. This gas is purified by the "scrubbers" *C* and *D*, containing dry coke and coke wet with sulphuric acid, respectively. **Arsenic**, which is usually present in the pyrites, and which **must be removed** to make the process successful, is removed in the "arsenic purifier" (*E*). In *H* the

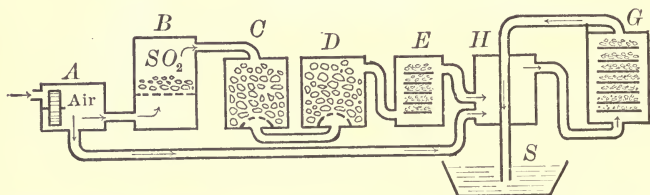


FIG. 59.

sulphur dioxide is mixed with air, and the mixture is heated. The amount of air used is such that there is a *large excess of oxygen*, in order that the "mass action" of the oxygen (*cf.* § 246) may make the change to sulphur trioxide as complete as possible. The heated gases then pass to the "contact chamber" (*G*), in which combination is effected. The resulting sulphur trioxide is absorbed in concentrated (i. e., 97–98%) sulphuric acid. The trioxide unites with the small amount of water present to give the acid. The acid is kept at the required concentration by the addition of water.

262. Chamber Process.—In the Chamber process sulphur dioxide, produced from pyrites or crude sulphur, is conducted into large boxes lined with lead, and called the "lead chambers." Air and

steam are also forced in, and nitric acid is introduced from time to time. *Dilute sulphuric acid* is the result.

Explanation. — The nitric acid introduced into the leaden chambers is reduced to *nitric oxide*, NO; a small amount of sulphur dioxide is thus oxidized directly by nitric acid. But the greater portion of the oxygen used comes from the air; for

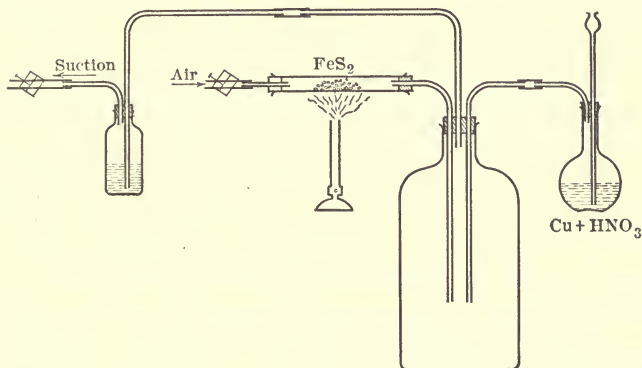


FIG. 6C.

the nitric oxide takes up the oxygen of the air, forming nitrogen dioxide (cf. § 237), and then gives up the oxygen to the sulphur dioxide. All of these facts are represented by the following equations: —

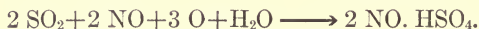
- (1) $\text{SO}_2 + 2 \text{HNO}_3 \longrightarrow \text{H}_2\text{SO}_4 + 2 \text{NO}_2$.
- (2) $\text{NO}_2 + \text{SO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + \text{NO}$.
- (3) $2 \text{NO} + \text{O}_2 \longrightarrow 2 \text{NO}_2$.
- (4) Repetition of (2).

Theoretically, a very small amount of nitric acid ought to be able to oxidize an indefinitely large

amount of sulphur dioxide, but in practice some of the nitrogen oxides are lost; hence, nitric acid must be added from time to time to the mixture in the leaden chambers. The greater portion of the nitrogen oxides is prevented from escaping by being made to pass through towers of concentrated sulphuric acid, which absorbs them. They are then returned to the leaden chambers to perform again the work of oxidizing sulphur dioxide.

The equations given above are only incomplete representations of the reactions taking place in the leaden chambers.

It is *probable* that the nitric oxide reacts with the steam, oxygen and sulphur dioxide present in the leaden chambers, giving a substance called *nitrosyl sulphuric acid*. The equation is, —



The nitrosyl sulphuric acid is a solid substance. It is known technically as “chamber crystals.” It is readily decomposed by the excess of steam, giving sulphuric acid and nitrogen trioxide (N_2O_3), as is shown by the equation, —



Apparatus for demonstrating the nitrosyl sulphuric acid manufacture is shown in Fig. 60.

263. Purification of Sulphuric Acid. — The sulphuric acid obtained in the leaden chambers contains about 35% of water; it is, therefore, concentrated by evaporation. The evaporation is carried out in *leaden pans* until the acid is concentrated

enough to attack the lead. When this is the case, further evaporation is carried out in *cast-iron* pans until an acid containing about 13% of water is obtained. This is the "crude" sulphuric acid of commerce. It is very impure. If the acid is to be concentrated still further, the evaporation must be carried out in vessels of *glass, porcelain, or platinum*.

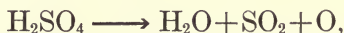
The pure acid is made by distilling the crude product in stills of platinum lined with gold. There is thus obtained an oil boiling at 338° C. and containing only 1.5% water. Its specific gravity is 1.854 at 0° C. The anhydrous acid (approximately 100% sulphuric acid) is made only in very small amounts.

264. Properties. — Sulphuric acid is a thick, oily, colorless liquid. When it is diluted with water, much heat is evolved, so much, indeed, that the water sometimes boils. To avoid spattering of the hot liquid we pour the concentrated acid in a small stream *into the water*, not the water into the acid.

Sulphuric acid forms several **hydrates** with water, the two most important being those represented by the formulas, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 2 \text{H}_2\text{O}$. Because of the tendency of sulphuric acid to take up water, it is used as a *drying agent*.

The dehydrating power of sulphuric acid also accounts for the fact that organic matter, *e. g.*, paper, wood, dust, sugar, etc., are *charred* by it. These bodies are compounds containing carbon, hydrogen, and oxygen (*cf.* § 543). The hydrogen and oxygen are abstracted, *as water*, by the acid, and charcoal is left.

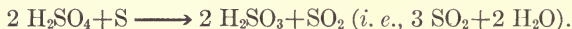
265. Reduction of Sulphuric Acid. — Sulphuric acid decomposes, when sufficiently heated, much as nitric acid does; the products are chiefly sulphur dioxide, oxygen, and water. The equation, —



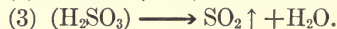
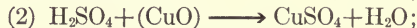
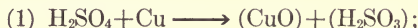
thus represents what takes place. If we have at hand a substance that can combine with oxygen, the decomposition of the acid takes place very easily. The reducing agents may be sulphur, charcoal, copper, mercury, etc.

The acid has no action upon these substances in the cold; but when it is heated with them the acid is reduced to sulphurous acid, *i. e.*, to sulphur dioxide and water. The reducing agents are, of course, oxidized.

For the action of **sulphur**, the equation is, —



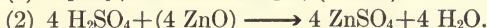
With **copper**, the *partial equations* are, —



The **complete** equation is, —



With **zinc**, the reduction is carried to **hydrogen sulphide**, if the layer of acid is very **thin**, so that the H_2S is not oxidized by the hot acid (*cf.* § 253).

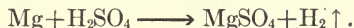
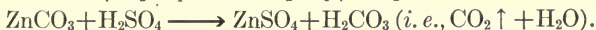


Hence, the *complete equation* is, —



266. Uses of Sulphuric Acid. — Sulphuric acid is made in *enormous* quantities. It is used in the preparation of *nitroglycerine* (§ 232), *nitric acid* (§ 223), *hydrochloric acid* (§ 126), and *coal-tar products* (§§ 232, 524, and 541). It is also used to *refine petroleum* (§ 525), to change starch into *glucose* (§ 545), to prepare **sodium carbonate** by the “Le Blanc” process (§ 414), and to convert the calcium phosphate of bone ash and of phosphate rocks into *soluble* form for use as **fertilizers** (§ 358). “The progress of civilization is proportional to the quantity of sulphuric acid used.”

267. Sulphates. — As sulphuric acid is dibasic (§ 166), it forms both *normal* and *acid* salts. The **normal** salts are formed by *neutralizing* basic hydroxides with dilute sulphuric acid, and by treating the oxides and carbonates of metals, or the metals themselves, with dilute sulphuric acid.

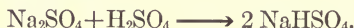


Acid sulphates (also called *bisulphates*) are obtained when *concentrated* sulphuric acid reacts with sodium chloride, sodium

nitrate, and sodium acetate to produce hydrochloric, nitric, and acetic acids, respectively (*cf.* §§ 126, 223, and 535). Acid sulphates are also formed when **one** equivalent weight of a metal hydroxide (*e. g.*, NaOH) reacts with **two** equivalent weights of the acid: —



They are, therefore, formed from many *normal* sulphates and **an excess** of sulphuric acid. Thus, when a solution of sodium sulphate is treated with dilute sulphuric acid, the *acid sulphate* is obtained (*cf.* § 259): —

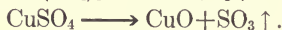
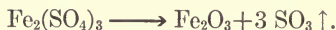


Barium sulphate and lead sulphate, which are insoluble in water, are “dissolved” by hot, concentrated sulphuric acid, as *acid sulphates*, —

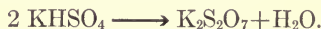


When the solutions are treated with water, the normal sulphates are precipitated. *Cf.* also § 88.

Stability of Sulphates. — Many sulphates are decomposed by heat, giving metal oxides, and either sulphur trioxide or its decomposition products, sulphur dioxide and oxygen (*cf.* § 222).



The acid sulphates of sodium and potassium give **pyrosulphates** when heated: —



Toward oxides of metals $\text{K}_2\text{S}_2\text{O}_7$ acts like $\text{K}_2\text{SO}_4 + \text{SO}_3$. Fused acid potassium sulphate is, therefore, used to clean platinum crucibles, by converting insoluble metal oxides into sulphates (*cf.* § 260).

Test for Sulphates. — We test for a *soluble* sulphate, *i. e.*, for SO_4 ions, by adding dilute hydrochloric acid and barium chloride solution, or dilute nitric acid and barium nitrate solution. If a white precipitate is formed, the solution taken probably contained a sulphate.



The *insoluble sulphates*, besides barium sulphate, are those of *lead* and of *strontium*. Calcium sulphate is *difficultly soluble* (*cf.* § 79).

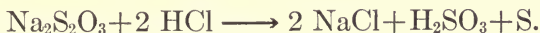
268. Thiosulphates. — *Thiosulphuric acid*, $\text{H}_2\text{S}_2\text{O}_3$, is sulphuric acid with one-fourth of its oxygen replaced by sulphur ("thion" = sulphur); its salts are called *thiosulphates*.

The most important thiosulphate is the sodium salt, $\text{Na}_2\text{S}_2\text{O}_3$. This is made by boiling a solution of sodium sulphite with sulphur.



This reaction corresponds to the oxidation of sulphites to sulphates (*cf.* § 259).

When sodium thiosulphate is treated with dilute acids, it breaks down as represented by the equation,



It decomposes, therefore, like a sulphite *plus* sulphur.

Sodium thiosulphate is a reducing agent capable of converting *chlorine* and *iodine* into *hydrochloric* and *hydriodic acids*, respectively. It is therefore used to destroy the excess of chlorine in the process of bleaching. It has the power to dissolve silver chloride, bromide, iodide, etc., and is, therefore, used in "fixing" negatives in photography. Its technical name is "hypo," from its *old* chemical name, "hyposulphite of soda."

269. Exercises.

1. How many grams of sulphur dioxide can be made by roasting 75 g. of iron pyrites? How many liters at 20° C. and 740 mm.?
2. How many grams ferrous sulphide are needed to give, with dilute sulphuric acid, 25 l. of hydrogen sulphide at 10° C. and 600 mm.?
3. How much sulphuric acid was there in a solution from which an excess of barium chloride precipitated 2.836 g. of barium sulphate? If the sulphuric acid was produced by the oxidation of the sulphur in 4 g. of a sulphur ore, calculate the per cent of sulphur in the ore.
4. How could you distinguish between sodium sulphide, sulphite, and sulphate? Between sodium, ammonium, and barium sulphates?
5. Would you use sodium sulphide in a Kipp's apparatus to give hydrogen sulphide? Cupric sulphide? Lead sulphide? Why?
6. Write the molecular equation for the burning of hydrogen sulphide in air. Give the relative volumes of all the gases used and produced.
7. What acid is formed by heating alum, and collecting the product in water (*cf.* § 222)? Alum and salt? Alum and niter? Alum, salt, and niter?

8. What drying agents may be used for sulphur dioxide? For hydrogen sulphide? What ones may not?

9. Silver sulphate is soluble. Write the equation for its action with barium chloride solution. Would you use barium chloride or nitrate, to test for its sulphate ions? Why?

10. How would you show that "heavy spar" is a sulphate (*cf.* §§ 252 and 254)?

11. Write the equation for the action of hot, concentrated sulphuric acid with mercury. With silver. With sugar (*cf.* § 543).

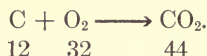
CHAPTER XXII.

CARBON AND ITS COMPOUNDS.

270. Carbon. — The element carbon is found in a free and an almost pure state as *diamond*, *graphite*, and *anthracite coal*; it is found *combined* in all *organic* substances, in *carbon dioxide*, in *carbonates*, in *coal*, and in *petroleum*.

Like sulphur, carbon exists in several *allotropic forms* (cf. § 249), the forms usually distinguished being (1) *diamond*, (2) *graphite*, and (3) *amorphous*, i. e., *non-crystalline*, carbon.

These three modifications of carbon differ to such an extent that they were long considered different chemical individuals. Their identity is proved by burning them in oxygen; for equal parts by weight of each give equal amounts of carbon dioxide.



271. The Diamond. — The diamond is prized for its luster, its strong refractive power, and its hardness. It is the hardest substance known.

The specific gravity of the diamond is 3.5. Acids and alkalies have practically no effect upon it; but when it is heated to about 700° C. in oxygen, it *burns*, forming carbon dioxide. When a diamond

is heated between the poles of a powerful battery it is changed into graphite.

Diamonds have been made artificially by crystallizing carbon *from solution in melted iron*. This process usually gives graphite, but if the melted iron cools under *great pressure* the carbon appears in the form of small diamonds. The necessary pressure is secured by chilling the exterior of the mass of iron; the contraction of the exterior thus causes great pressure upon the interior of the mass.

So far as known, no artificial diamonds yet made are large enough to have any commercial importance.

272. Graphite. — Graphite is sometimes found crystallized, but usually in an amorphous form. Its specific gravity is about 2.25. It owes its name, "black lead," to a confusion of names.

Graphite is a good conductor of heat and of electricity. Owing to its *friability* it is used to make "lead" pencils. Mixed with clay it is the material of graphite crucibles, which are used in making "crucible" steel. Other uses are: To protect iron from the air, as in stove polish, to coat grains of shot, and as a lubricant.

Graphite is produced artificially (*cf.* § 271) by crystallizing charcoal from molten iron and steel.

273. Amorphous Carbon. — The amorphous forms of carbon include the several varieties of coal, gas carbon, coke, charcoal, and lampblack; all of these

are formed by the *charring*, i. e., carbonization, of animal or vegetable substances.

274. Natural Carbonization; Coal. — Carbonization has taken place in nature on a large scale. Vegetable matter, accumulated in certain localities through many generations, and decaying in the absence of air, was without doubt the material from which coal was formed. This partially decayed matter was probably much like *peat*. When the peat was buried under sediments, and thus subjected to water and pressure, a slow carbonization took place; as a result gaseous products, such as natural gas, etc., passed off, and the *excess* of carbon remained behind.

The varieties of coal owe their origin to the different degrees of water-action and pressure to which the peat was subjected. Thus, soft, i. e., bituminous, coal contains many gaseous substances, as is shown by its burning with a large flame and much smoke; anthracite coal, on the contrary, is nearly pure carbon, and burns with a *small* flame.

The table on the following page shows the *approximate* composition of wood and of several varieties of coal. The difference between the sum of the parts per cent and 100 represents in each case the *ash*, or mineral matter, of the coal.

275. Artificial Amorphous Carbon. — The artificial carbonization of wood produces *wood charcoal* and

lampblack; that of soft coal, *coke* and *gas carbon*; that of animal matter (bones, blood, etc.), *animal charcoal* and *bone-black*.

	PER CENT OF			
	CARBON.	HYDROGEN.	OXYGEN.	NITROGEN.
Wood.	50	6.0	43	
Peat.	62	5.7	32	
Lignite.	68	5.7	25	About 1.
Bituminous.	79	5.3	14	About 1.
Cannel.	83	7.0	9	About 1.
Anthracite.	92	3.5	3	About 1.

Lampblack. — Lampblack, or *soot*, is produced by burning resinous wood, or, for the better grades, oil or gas, in an insufficient supply of air. It is used in making printer's ink, black paints, India ink, etc.

Wood Charcoal. — Wood charcoal is made by the "destructive distillation" of wood. The operation may be carried out either in iron retorts, or by piling the wood in heaps covered with sod (Fig. 61), and then setting fire to the heaps. In the latter case *some* of the wood burns, but its combustion gives heat for the decomposition of the remainder.

The charcoal obtained from a given mass of wood weighs from 15% to 25% as much as the wood taken; the loss is due

to the escape of volatile substances. The gaseous products were formerly used as illuminating gas; the liquid parts consist of wood spirit (methyl alcohol), acetic acid, etc.

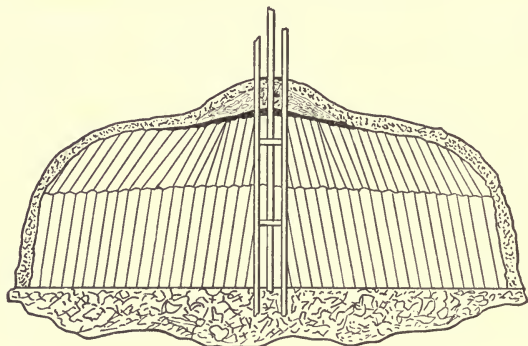


FIG. 61.

Wood charcoal is used in the reduction of iron from its ores and as a disinfectant. It absorbs large quantities of certain gases: ninety volumes of ammonia or nine volumes of oxygen are known to have been taken up by one volume of box-wood charcoal. Charcoal owes its action as a disinfectant to its power of absorbing noxious gases, along with oxygen, in its pores. The oxygen destroys the bacteria in the other gases.

Coke and Gas-Carbon. — *Coke* is the residue left when soft coal is distilled; *gas-carbon* is the volatile coke condensed upon the walls of the retorts.

Gas-carbon is *metallic* in character and a good conductor of electricity; it is used for the negative plates of electric cells and for the pencils of electric arc-lamps.

Coke is used chiefly in metallurgy to reduce the metals from their ores. It is also a fuel.

The volatile products obtained in the distillation of coal consist of illuminating gas, coal-tar (the source of many organic compounds), ammonia, etc. (*cf.* § 204).

Animal Charcoal and Bone-black. — Animal charcoal and bone-black are used to destroy organic coloring matter. When a solution of brown sugar, for example, is filtered through bone-black, the solution becomes colorless. Vinegar may be clarified in the same way.

When bones are distilled destructively the volatile products consist largely of *bone-oil*. Usually the bones are deprived of their gelatine before being carbonized. In either case the animal charcoal obtained contains the mineral matter of the bones.

276. Carbon Dioxide; Occurrence. — There are two compounds of carbon and oxygen, viz., *carbon monoxide* and *carbon dioxide*; of these the latter is by far the more important.

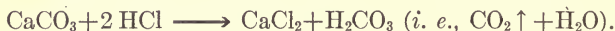
Carbon dioxide is present in the air, in some mineral springs, and in certain localities where it escapes from the earth. Ten thousand parts by volume of air contain, on the average, about 3.5 parts of carbon dioxide (*cf.* § 193).

Carbon Dioxide Exhalations. — At Herste, near Driburg, Germany, certain borings made in 1894 struck carbon dioxide at a depth of 148.5 meters. A violent outburst of the gas took place, no less than 40,000,000 liters escaping daily. The carbon

dioxide was 99.84% pure. Thousands of kilograms were liquefied daily.

The origin of the carbon dioxide was probably the action of certain silicates, *i. e.*, salts of *silicic acid*, H_2SiO_3 , upon calcium carbonate.

277. Preparation of Carbon Dioxide. — In the laboratory, carbon dioxide is commonly made by decomposing a carbonate by an acid. The carbonate generally used is *marble*, CaCO_3 . The reaction of marble with hydrochloric acid is represented by the equation, —



Evaporation of the solution, after all action ceases, gives calcium chloride, CaCl_2 , the substance used to dry gases, etc.

278. Physical Properties. — Carbon dioxide is a colorless gas. It has the slightly acid taste known to all who drink “soda water.” It is about one and one-half times as heavy as air; one liter weighs 1.97 g. under standard conditions.

Gaseous carbon dioxide may be condensed to the liquid state at *ordinary* temperatures by a pressure of about fifty atmospheres; above 31°C. , however, — its critical temperature, — the gas cannot be liquefied by pressure. If liquid carbon dioxide is allowed to evaporate rapidly, it solidifies, forming a white mass like snow. When liquid air (*cf.* § 198) evaporates, solid carbon dioxide is usually left behind.

About ten million kilograms of liquid carbon dioxide are used annually.

Water absorbs about 1.8 times its own volume of carbon dioxide under standard conditions; with increase of pressure the amount *increases* (cf. § 83). When the excess of pressure is removed from water *surcharged* with carbon dioxide, much carbon dioxide escapes; hence the sparkling of "soda water," and also of spring water, which usually has carbon dioxide in solution.

279. Chemical Properties. — Carbon dioxide does not allow ordinary burning to continue in it any more than water does, and for the same reason.

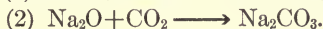
Because of its inability to support combustion, carbon dioxide is used to extinguish fires. For this purpose it is generated in a strong reservoir by the action of dilute sulphuric acid upon sodium carbonate.



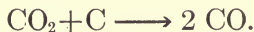
The resulting gas is directed in a stream upon the flames.

Very *strongly* burning substances, however, continue to burn in the gas; examples are *sodium* and *magnesium*.

The equations for the action of burning sodium upon carbon dioxide are, —



When carbon dioxide is passed over red-hot carbon (Fig. 62) it is reduced to carbon monoxide (*cf.* § 286).



The *volume* of the carbon dioxide formed by the union of a given volume of oxygen with carbon is

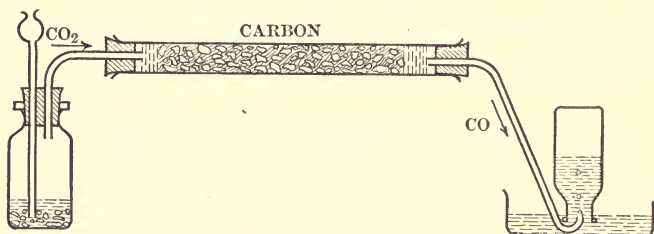


FIG. 62.

equal to the volume of the oxygen. Or we may state it thus: A *gram-molecular volume* of oxygen gives a *gram-molecular volume* of carbon dioxide (*cf.* § 145).



Of the volume of the carbon nothing can be stated because carbon cannot readily be obtained in the gaseous state.

280. Other Sources and Uses of Carbon Dioxide.

— (a) **Fermentation.** When an aqueous solution of cane sugar or grape sugar is subjected to the action of the yeast plant, the sugar is decomposed; the chief products are *ethyl alcohol*, $\text{C}_2\text{H}_5\text{OH}$, and carbon

dioxide. The alcohol remains in solution, but most of the carbon dioxide escapes in gaseous form.

Fig. 63 shows some characteristic yeast plants in the process of budding.

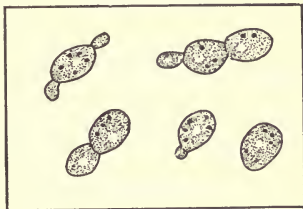


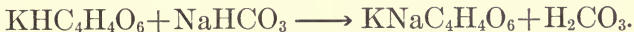
FIG. 63.

The decomposition of sugar by yeast is called *alcoholic fermentation*. Grape sugar is a complex compound of the formula $C_6H_{12}O_6$; its decomposition in fermentation is *chiefly* according to the equation, —



The brewer uses fermentation to produce alcoholic liquors; the baker, to *raise* bread.

(b) **Baking Powders.** — Ordinary baking powder is a mixture of *potassium hydrogen tartrate*, $KHC_4H_4O_6$ (commonly called “cream of tartar”), and *sodium bicarbonate*, $NaHCO_3$, with some diluting substance, *e. g.*, corn-starch. The ingredients act upon each other only when moist or in solution. The equation for the decomposition of baking powder is, —



The substance $KNaC_4H_4O_6$ is called “Rochelle Salt.”

Theoretically, any substance that will liberate carbon dioxide from sodium bicarbonate might be used in place of cream of tartar, but practically a substance must be used that will not form a residue injurious to the human system.

“ Acid Phosphate ” baking powders contain sodium bicarbonate and *calcium hydrogen phosphate*, $\text{CaH}_4(\text{PO}_4)_2$. The calcium hydrogen phosphate liberates carbon dioxide from sodium bicarbonate, just as cream of tartar does.

281. Relation of Carbon Dioxide to Life. — Substances containing carbon usually give by their oxidation carbon dioxide. The same result follows whether the oxidation is slow or rapid. Hence all *decay*, as of wood, paper, etc., results in the formation of this gas.

Carbon dioxide fails to support animal life, not because carbon dioxide is *poisonous*, but because animals cannot extract from it the oxygen necessary for respiration. Besides, the presence of even a little more than the normal amount of carbon dioxide in the air, say, 7 or 8 parts in 10,000, prevents the proper exit of carbon dioxide from the lungs.

The fact that the enormous quantity of carbon dioxide constantly poured into the air by the respiration of animals and plants does not accumulate until it destroys higher animal life is due largely to the agency of vegetation.

To plants, carbon dioxide is an important *food*; for chlorophyll-producing, i. e., *green*, plants are able

to convert carbon dioxide and water, *in the presence of light*, into sugar, starch, wood, and the various compounds of carbon, hydrogen, and oxygen of which most vegetable products consist.

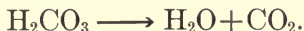
The natural *cycle* through which carbon dioxide passes is as follows: —

(1) Plants, by means of energy derived from the sun, change carbon dioxide and water into plant tissue;

(2) Animals, appropriating the stored-up energy of plants, give it forth in their activities and return carbon dioxide to the air.

282. Carbonic Acid. — The aqueous solution of carbon dioxide has slightly acid properties and gives *carbonates* with soluble bases; hence the substance H_2CO_3 — *carbonic acid* — probably exists in solution. Carbon dioxide is thus *carbonic anhydride*.

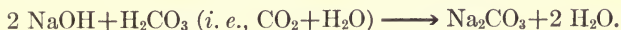
Carbonic acid cannot be isolated; for it breaks up very readily into carbon dioxide and water.



In its instability carbonic acid is like ammonium hydroxide and sulphurous acid (*cf.* §§ 203 and 259).

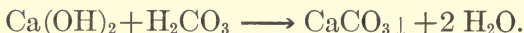
283. Carbonates. — When carbon dioxide is passed into solutions of metallic hydroxides it is absorbed, forming *carbonates*.

Thus, sodium hydroxide and carbonic acid (carbon dioxide with water is probably *carbonic acid*) react according to the equation,

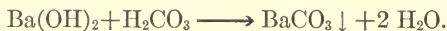


A similar reaction takes place when carbon dioxide is passed into a solution of calcium hydroxide (lime-water); but in this case the carbonate formed is *insoluble*. As a result the lime-water becomes "milky."

The equation is, —



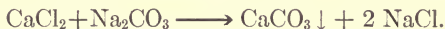
With *baryta-water* (barium hydroxide solution) the result is analogous.



If a gas forms a white precipitate on being passed into lime-water or baryta-water, we generally assume that the gas is carbon dioxide (cf. § 193).

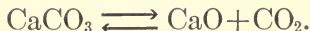
All the common carbonates except those of sodium, potassium, and ammonium are *insoluble* in pure water, and are, therefore, *precipitated* when one of the three soluble carbonates is added to the solution of a metal salt.

Thus, *sodium carbonate* gives with *calcium chloride* a precipitate of *calcium carbonate*.



Most carbonates except those of sodium and potassium decompose, when heated, into the corresponding oxides and carbon dioxide.

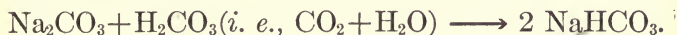
Thus, marble gives, when heated, quicklime and carbon dioxide. These *recombine* when cold.



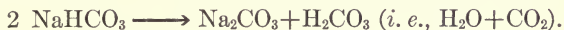
Ammonium carbonate is, of course, decomposed by heat, like other ammonium salts. It is often called "*sal volatile*."

The common method of *identifying* a carbonate is to treat it with a dilute acid and then to prove that the escaping gas is carbon dioxide.

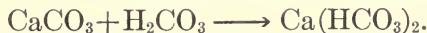
284. Bicarbonates. — If carbon dioxide is passed into lime-water long enough, the precipitate of calcium carbonate, which is formed at first, will be *redissolved*. A similar result takes place with barium hydroxide. This phenomenon may be best understood by comparing it with the action of carbonic acid (*i. e.*, carbon dioxide and water) upon sodium carbonate (*cf.* § 267) — a reaction represented by the equation,



The substance NaHCO_3 is *sodium hydrogen carbonate* (called, also, sodium bicarbonate); when it is heated gently it breaks up into sodium carbonate, carbon dioxide, and water.



In a similar way an excess of carbonic acid converts calcium carbonate into *calcium hydrogen carbonate*, $\text{Ca}(\text{HCO}_3)_2$. The precipitate of calcium carbonate redissolves, therefore, owing to the formation of *calcium bicarbonate*, which is soluble. The equation is, —



Calcium bicarbonate is, however, *very unstable*; it decomposes, when its solution is heated, into calcium



FIG. 64.

carbonate, carbon dioxide, and water. *Hence the precipitate of calcium carbonate reappears on boiling.*

The behavior of calcium carbonate with an excess of carbon dioxide explains the solubility of limestone in natural waters which contain this gas; and the ease with which calcium bicarbonate is decomposed explains why most waters deposit their limestone upon the walls of vessels in which they are heated (*cf.* § 70).

In many limestone regions underground waters are charged under pressure with carbon dioxide, and therefore take up large quantities of limestone; subsequently the carbon dioxide escapes, and the limestone is deposited. These limestone deposits often take on beautiful and fantastic forms, as *stalactites*, etc. See Fig. 64.

285. Natural Carbonates. — The most abundant natural carbonate is *limestone*, CaCO_3 . Large quantities of this substance are distributed over the land and in the sea.

Marble is a finely crystallized limestone. *Iceland spar* is almost pure calcium carbonate; it occurs in large crystals. *Coral* is limestone taken from the sea by the coral polyp and left as a residue when the polyp dies. The *shells* of most water animals are largely limestone.

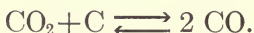
A natural mixture of calcium and magnesium carbonates called *dolomite* is also very abundant; it is the chief component of whole ranges of the Alps mountains. *Magnesite* is natural magnesium carbonate.

Sodium carbonate and *potassium carbonate* exist in the soil of many places. The ashes of sea-plants contain sodium carbonate; those of land-plants, potassium carbonate.

Both of these carbonates are used in large quantities and are made *synthetically*, especially sodium carbonate, on an enormous scale (*cf.* § 414). A large and valuable deposit of almost pure sodium carbonate occurs at Owen's Lake, California.

286. Formation of Carbon Monoxide. —

Carbon monoxide is produced by the reduction of carbon dioxide by red hot carbon (*cf.* Fig. 62). The reaction is reversible.



A common illustration of the same reaction is seen in every coal fire. The coal at the bottom (Fig. 65) burns to carbon dioxide; but as this gas passes through the bed of heated coal it is reduced to carbon

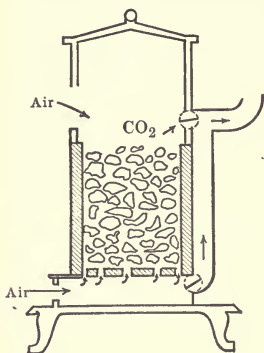


FIG. 65.

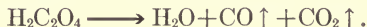
monoxide. The carbon monoxide then burns at the top of the bed of coal to carbon dioxide.



287. Laboratory Method. —

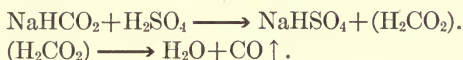
The common method of preparing carbon monoxide is to heat crystallized oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$, with concentrated sulphuric acid.

The sulphuric acid removes both the water of crystallization and the water formed by the decomposition of the oxalic acid.



The carbon dioxide is removed by passing the gases through sodium hydroxide solution, with which the carbon monoxide does not combine.

Sodium formate and concentrated sulphuric acid give, first, **formic acid**, and then carbon monoxide.



Another method of making carbon monoxide is to heat *potassium ferrocyanide*, $\text{K}_4\text{Fe}(\text{CN})_6$ (called, also, "*yellow prussiate of potash*"), with concentrated sulphuric acid.

288. Properties. — Carbon monoxide bears to *formic acid*, H_2CO_2 , a relation similar to that which carbon dioxide bears to *carbonic acid*. This is evident from the formulas.

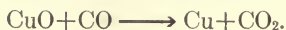
Formic acid, H_2CO_2 . *Carbon monoxide*, CO .
Carbonic acid, H_2CO_3 . *Carbon dioxide*, CO_2 .

Water and carbon monoxide do not unite, however, under ordinary conditions. When carbon monoxide is passed over sodium hydroxide at 160°C ., the two combine to give *sodium formate*: —



Carbon monoxide is a colorless gas; when pure it is almost odorless. It is popularly known as "*coal gas*," and is familiar to every one who has used anthracite coal. It burns with a beautiful, blue flame, giving carbon dioxide. The flame is best observed when fresh coal is put upon a hot fire.

Because of the ease with which it is oxidized, carbon monoxide is a powerful **reducing agent** (*cf.* § 482).

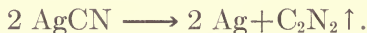


Unlike carbon dioxide, carbon monoxide is *extremely poisonous*; air containing one per cent of it will produce fatal results.

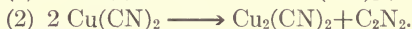
One liter of carbon monoxide weighs 1.25 g. under standard conditions. The gas has been liquefied at -141°C. , its critical temperature, by a pressure of 35 atmospheres.

289. Cyanogen. — Carbon and nitrogen combine to form a gas called *cyanogen*, C_2N_2 . Cyanogen may be prepared by heating *mercuric cyanide*, $\text{Hg}(\text{CN})_2$, or silver cyanide, AgCN .

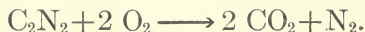
With silver cyanide the equation is, —



A cheaper way is to allow a solution of *potassium cyanide*, KCN , to fall drop by drop into a hot solution of cupric sulphate. *Cupric cyanide*, $\text{Cu}(\text{CN})_2$, is first formed, but at once breaks up into *cuprous cyanide*, $\text{Cu}_2(\text{CN})_2$, and cyanogen.

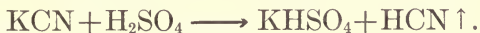


Cyanogen is a colorless, sweet-smelling gas. It burns with a beautiful, lavender-colored flame, forming carbon dioxide and nitrogen.



Cyanogen is *so poisonous* that no one but an experienced person should make it in quantity, and then only where there is a *strong draught*.

290. Hydrocyanic Acid. — Hydrocyanic, or *prussic*, acid is extremely poisonous. It may be made by treating *cyanides*, e. g., potassium cyanide or potassium ferrocyanide, with dilute sulphuric acid.



It is a colorless, sweet-smelling liquid, boiling at 27°C .

291. Compounds of Carbon and Hydrogen. — The number of compounds formed by carbon and hydrogen is very large. At present we shall consider only *four*, viz.: *methane*, CH_4 ; *ethane*, C_2H_6 ; *ethylene*, C_2H_4 , and *acetylene*, C_2H_2 . All are colorless gases.

292. Methane. — Methane, or *marsh gas*, is formed in the destructive distillation of coal, and is, therefore, present in illuminating gas made by the old process (*cf.* § 297). It is formed in nature by the decay of organic matter, e. g., leaves, twigs, etc., under water; hence the name “marsh gas.” The presence of the gas may be observed by disturbing the material at the bottom of most stagnant pools, especially in summer.

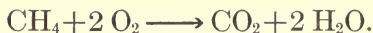
Marsh gas also enters coal mines; here its mixture with air forms the dreaded "*fire damp*" (damp = gas; cf. Ger. Dampf.), which explodes with frightful violence when ignited. It was to avoid these explosions in mines that Davy made his celebrated "*safety lamp*" (cf. § 30).

Methane forms over ninety per cent of the gases that escape from petroleum wells.

Marsh gas is commonly made in the laboratory by heating a mixture of *sodium acetate*, $\text{NaC}_2\text{H}_3\text{O}_2$, *sodium hydroxide*, and *quicklime*.• The gas thus produced is not pure, however; it contains *hydrogen* and other impurities. An *approximate* equation is, —



The equation representing the combustion of marsh gas is, —



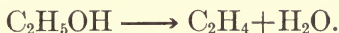
293. Ethane. — Ethane is formed along with marsh gas in the decomposition of many organic substances, and is a constituent of illuminating gas. Its composition is represented by the formula, C_2H_6 . It burns with an almost colorless flame.

In burning, ethane produces carbon dioxide and water, just as marsh gas does, but the relative proportions are different. This fact is shown by the equation, —

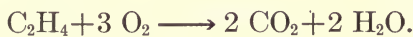


294. Ethylene.• — Ethylene may be prepared by heating ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, with concentrated

sulphuric acid to above 140° C. The following equation represents *in part* what takes place: —



Ethylene is present in illuminating gas; it burns with a bright, *luminous* flame, producing carbon dioxide and water.



The most remarkable property of ethylene is its power to absorb chlorine and bromine, giving ethylene chloride and bromide.



Both the chloride and the bromide are heavy, colorless oils.

295. Acetylene. — Like the other compounds of hydrogen and carbon that have been mentioned, acetylene is present in illuminating gas. It is formed when a Bunsen burner burns at the base instead of at the top, and may then be recognized by its penetrating odor.

Acetylene has been formed by passing an electric spark between carbon terminals in a vessel of hydrogen.



Acetylene is now made on a commercial scale by the action of water containing a little hydrochloric acid upon the *carbides* of certain metals. The carbide commonly used is *calcium*

carbide, CaC_2 . The decomposition of this substance by water is represented by the equation, —

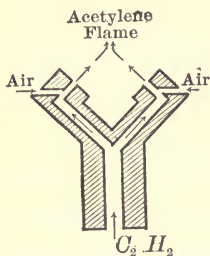
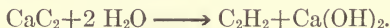
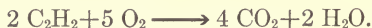


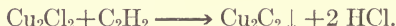
FIG. 66.

In the air, acetylene burns with a very smoky flame. With a proper burner the flame is of dazzling whiteness and without soot.



Acetylene is readily condensed to the liquid state. Ordinary mixtures of gaseous acetylene and air are very explosive.

When acetylene is passed into solutions of *cuprous* and of *silver* salts containing an excess of ammonium hydroxide, “**acetylides**” are precipitated.



These are explosive when dry. If treated with *excess* of hydrochloric acid, they give back acetylene.

296. Illuminating Gas. — Illuminating gas is a mixture of several gases already studied. These gases may be divided into (a) *combustible* gases and (b) *impurities*.

The impurities are chiefly *nitrogen* and *carbon dioxide*.

The combustible gases are of two kinds: —

(1) Those that burn without giving light, and (2) those that burn with luminous flames.

The *non-illuminating* gases are *hydrogen*, *methane*, and *carbon monoxide*; they make up about ninety per cent by volume of the gas. The *illuminating* gases are the so-called "heavy hydrocarbons," *ethane*, *propane*, C_3H_8 , *butane*, C_4H_{10} , etc., and, usually, small amounts of *ethylene* and *acetylene*.

Two general processes are employed in making illuminating gas:—

- (1) The distillation of soft coal.
- (2) The "water-gas" process.

297. Illuminating Gas by Distillation of Coal. —

The *old* process of making gas is carried out as shown in Fig. 67.

Soft coal in the retorts (there are usually several retorts, one over the other) is heated by the furnace to the temperature of decomposition. The volatile products pass off through a pipe

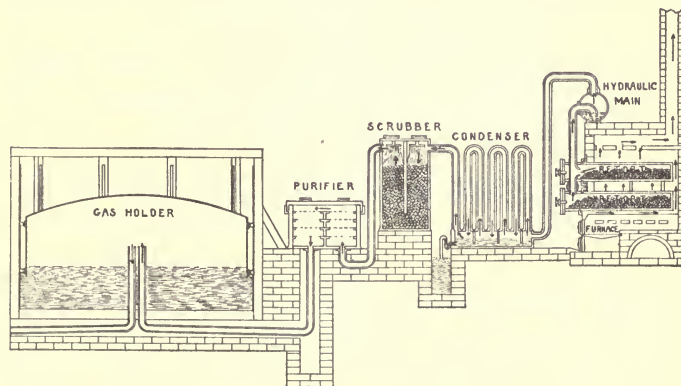


FIG. 67.

into the "hydraulic main." The hydraulic main contains water, which condenses much *tar*, etc., from the gas. From the main the gas passes through the "condenser," which stands over water; here the gas is cooled, and more of the tarry products are condensed.

From the condenser the gas passes through the coke tower, or "scrubber"; into this water is sprayed, and the illuminating gas is thereby freed from *soluble* gases, such as *ammonia* and *hydrogen sulphide*.

From the "scrubber" the gas passes into the "purifier."

The purifier is a large box containing trays of slaked lime; this substance removes carbon dioxide and traces of hydrogen sulphide. The gas then enters the gas holder; thence it is distributed to the community through the service pipe.

Many other valuable products besides illuminating gas are obtained by the distillation of coal. The ammoniacal liquors of the condensers and coke towers are the sources of *ammonium* compounds (*cf.* § 204); the tar of the hydraulic main and condensers gives, when distilled, the important substances *benzene*, *toluene*, *phenol* (carbolic acid), *naphthalene*, etc.; the residue in the retorts is *coke* and *gas carbon* (*cf.* § 275).

The composition of a representative illuminating gas made by the old process is shown in the table accompanying § 299.

298. Water-gas Process. — Within recent years the old process for the production of artificial gas has been almost entirely displaced by the "water gas" process. In this process steam is passed over

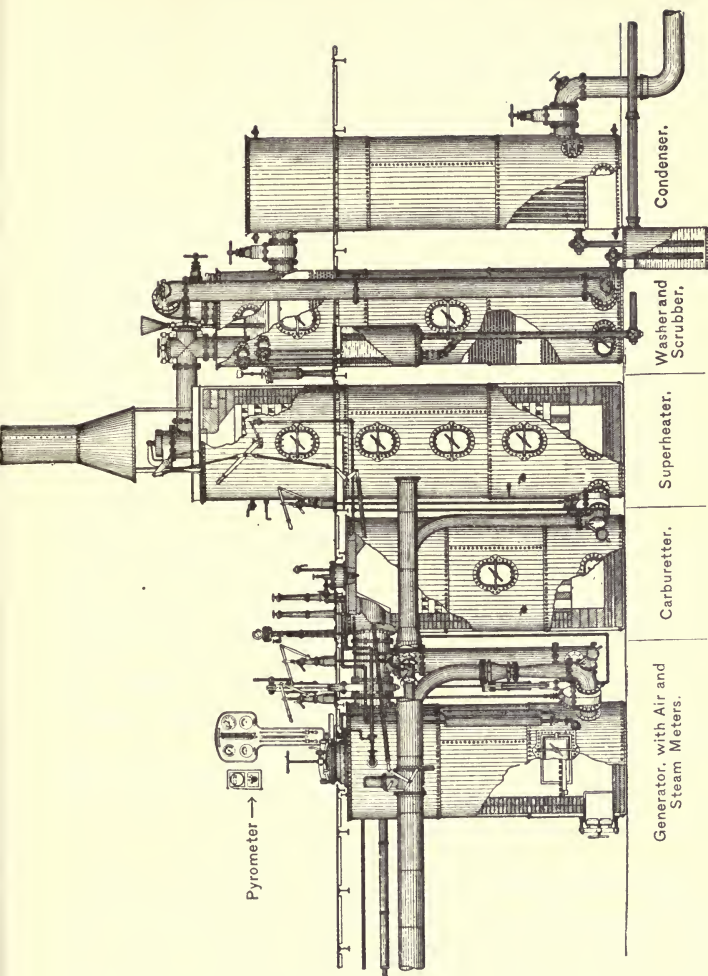
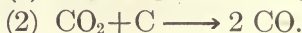
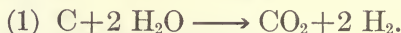


FIG. 68.

DOUBLE SUPERHEATER LOWE WATER GAS APPARATUS FOR CARBURETTED WATER GAS.

white-hot anthracite coal. The reactions which take place are represented by the equations, —



The mixture of carbon monoxide and hydrogen is “water-gas.” It may be used directly for fuel, but not for lighting, since it burns with a colorless flame.

For the conversion of water-gas into an illuminating gas, the water-gas is “enriched” by the addition of petroleum hydrocarbons. The process of making an illuminating water-gas will be understood from Fig. 68.

Anthracite coal is heated to white heat in the “generator” by means of a blast of air forced through the coal by a “blower.” The blast of air is then cut off, and superheated steam is forced over the coal, reacting with it, as already shown, to form carbon monoxide and hydrogen. The mixture of these two gases is then forced into the “superheaters,” in which light petroleum oils are being decomposed by heat. Here the water-gas obtains marsh gas and the hydrocarbons which give ordinary gas its illuminating power.

From the superheaters the gas passes through the “scrubber” and the “condenser,” in which the undecomposed petroleum and any carbon dioxide, etc., are removed.

299. Comparison of the Two Kinds of Gas.—

The composition of two samples of illuminating gas, one made by the distillation of coal and the other by the “water-gas” process, is given in the following table: —

	OLD PROCESS.	NEW PROCESS.
Hydrogen.	46.0%	29.5%
Methane.	39.0%	20.0%
Carbon monoxide.	5.5%	32.7%
Hydrocarbons.	6.0%	11.2%
Carbon dioxide.	1.2%	2.8%
Oxygen.	0.3%	0.0%
Nitrogen (by difference).	2.0%	3.8%
Total.	100.0%	100.0%

Gas made by the "water-gas" process is more poisonous than that made by the distillation of coal, owing to the presence of so much carbon monoxide in water-gas; otherwise the gases are much alike. The quantity of manufactured gas used in the United States is about 100,000 millions of cu. ft. annually. Chicago, alone, used more than 17,000 millions of cu. ft. of it in 1911.

300. Pintsch and Producer Gases.

Pintsch gas is an illuminating gas made by "cracking," or decomposing, petroleum through contact with bricks at 1000° C. (*cf.* § 298). It must be burned with a special burner, as must acetylene, but it has great illuminating power. It is stored in steel cylinders, under pressure, and is used in lighting railway cars.

Producer gas is a *fuel* gas made by passing air through white hot coke or coal. It usually has about 30% of carbon monoxide, the remainder being the nitrogen of the air, and carbon dioxide formed by oxidation of some of the carbon monoxide.

301. Exercises.

1. How many grams of carbon are needed to reduce 15 grams cupric oxide, CuO , if the carbon is oxidized to carbon dioxide? How many grams of carbon dioxide are formed?

2. What volume of carbon dioxide at 30°C . and 730 mm. can be produced from 840 grams magnesium carbonate, MgCO_3 ?

3. How many grams of sodium bicarbonate are needed to give, *when heated*, 36 liters of carbon dioxide? (Cf. § 284.)

4. If 50 l. of water-gas (§ 299) were burned, how many grams of water and carbon dioxide would result? Use standard conditions, and consider "hydrocarbons" to be *ethane*.

5. How many liters of carbon dioxide are formed, under standard conditions, by the combustion of 250 grams carbon monoxide?

6. Calculate the percentage composition of calcium carbonate, carbon dioxide, oxalic acid.

7. How would you distinguish between sodium carbonate, sulphite, sulphide, and formate, chemically?

8. How would you distinguish between the gases carbon dioxide, carbon monoxide, oxygen, hydrogen, and ammonia?

9. Calculate the volume, in liters under standard conditions, of 10 g. of each of the following: *methane*, *ethane*, *ethylene*, and *acetylene*.

Calculate also the volume of oxygen needed, and the volumes of steam and carbon dioxide produced, in the combustion of 10 g. of each of these gases. Use standard conditions.

CHAPTER XXIII.

FLAMES, LIGHT, AND HEAT.

302. Luminosity of Flames. — As stated in Chapter II, § 28, *a flame is a burning gaseous body*. The amount of light given off by a flame depends upon the *nature* of the burning substance and upon its *density*.

As an illustration of the influence of density, we may take the case of hydrogen. This substance ordinarily burns in air and in oxygen with an almost invisible flame; if, however, the hydrogen and the oxygen are very much compressed before ignition, the flame produced by their union is a very brilliant one.

The illuminating power of all ordinary flames is due to the presence of *incandescent solid particles*. This may be illustrated by introducing any fine dust into a flame of hydrogen or into the colorless Bunsen flame; the flame at once becomes luminous.

In the combustion of substances containing carbon, — such substances as candles, illuminating gas, paper, petroleum, wood, coal, etc., — the luminosity of the flame is due to the *glowing* of particles of carbon in the flame. A cold object inserted into the flame produced by one of these substances becomes covered with soot; and too little

air, or too much gas, causes the flame to smoke, owing to the escape of unburned particles of carbon.

303. Structure of Flames. — A burning candle shows practically the same phenomena as the other compounds of carbon just named, and may be taken as representative of them.

The burning of a small portion of the wick of the candle furnishes heat enough to melt some of the wax. The wick then draws the melted wax, by capillary action, into the flame, where it is vaporized and ignited.

If the candle flame be examined, it will be found to consist of several regions, or *zones*, of combustion, surrounding a central cone-shaped region of unburned gases. These parts are shown in vertical section in Fig. 69.

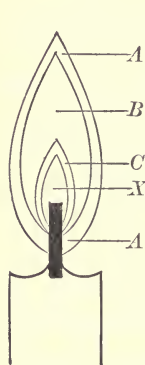


FIG. 69.

X is the region of unburned gases.

B is the luminous zone. It contains solid particles of carbon in a state of combustion.

A is the outer mantle of the flame. Being non-luminous it is obscured by the light of *B*, except at the bottom, where it forms a blue, cup-shaped region.

In addition to the parts just named, an important region (*C*) is believed to exist about the region *X*. Being non-luminous, the region *C* is obscured by the light of *B*.

Whether a flame is to be luminous or non-luminous depends upon the condition of affairs in the region *C*.

What takes place in a candle flame is probably as follows: —

The vaporized paraffin (wax) of the region *X* (Fig. 69) burns in part in the zone *C*, producing enough heat to decompose some of the paraffin vapor into hydrogen, certain hydrocarbons (especially acetylene), and solid carbon. These substances burn further in the region *B*, the carbon burning, as usual, with a bright *glow*, and thus causing the luminosity of this region. In *A* the gases and the carbon escaping unburned through *B* are more or less completely burned.

304. Non-Luminous Flames. — The decomposition of the combustible material of region *X* (Fig. 69) into acetylene, carbon, etc., in the region *C* requires a *definite degree of temperature*; hence, if the temperature of *C* is sufficiently lowered, the flame becomes non-luminous.

This is what takes place in a **Bunsen burner** (Fig. 70). When the holes are closed, the flame is luminous, and has the same regions as a candle flame. When the holes are opened, the gas rushing past the holes draws in air, the region *C* is **cooled**, and the flame becomes non-luminous. If carbon dioxide, nitrogen, etc., are introduced, instead of air, the result is the same.

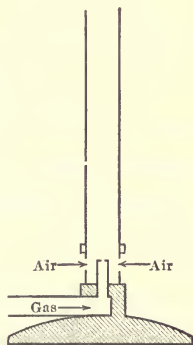


FIG. 70.

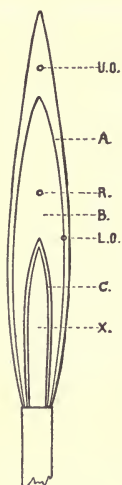


FIG. 71

The regions of a Bunsen flame are as follows (Fig. 71):

X is the region of unburned gas, as in the candle flame.

C is the light-blue, inner cone surrounding *X*.

B is the non-luminous, dark cone. In the candle flame this is luminous.

A is the purple, outer mantle. In the candle this is the faintly luminous *halo* surrounding the flame.

305. Heat and Light of Flames. —

The temperature of the different regions of a Bunsen flame varies greatly. In some parts it is probably 1500°C . If all the heat given off in the burning of carbon and hydrogen were used in raising the temperature, the flame would be hotter. As it is, a large part of the heat produced is used in decomposing hydrocarbons (§ 303) into carbon and hydrogen. For a similar reason the temperature of the oxyhydrogen blow-pipe flame (2800°C .) is far below what might be expected. At this temperature water is partly *dissociated* (cf. § 73); hence much of the heat evolved in the **union** of hydrogen and oxygen is used up again in decomposing steam.

Light from Incandescence.— The light-giving power of the electric incandescent lamp is due to the white-hot carbon, tungsten, or tantalum filament. In ordinary flames the source of light is *incandescent carbon* (§ 303). The hot, but colorless

oxy-hydrogen flame is made to produce light by heating lime (cf. § 55) to white heat. In the brilliant flames of burning magnesium and phosphorus (cf. § 24) the light is due to incandescent magnesium oxide and phosphorus pentoxide, respectively. The Bunsen burner may also be used to give light by heating solids to high temperatures. The **Welsbach** burner is a Bunsen burner with an incandescent "mantle." The "mantle" consists of the dioxides of **thorium** and **cerium** (and sometimes other oxides). The greatest light intensity results from a mixture of 99% ThO_2 and 1% CeO_2 .

306. Candle Power.

The standard of light intensity is the **candle power**. This is the illumination produced by a standard candle, burning 7.78 grams (120 grains) per hour. The candle power of some source of light, *e. g.*, an incandescent lamp, may be measured by means

of Rumford's *photometer* (Fig. 72).

The standard candle (of the size known as "sixes") and the lamp are made to throw two shadows of the vertical rod side by

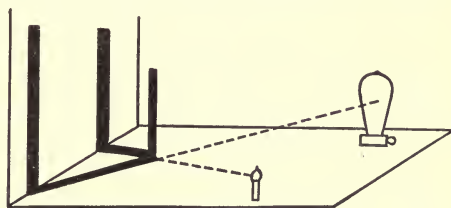


FIG. 72

side upon the screen. When the shadows are of equal density, the illumination from the two lights is equally intense. The intensity of light varies inversely as the square of the distance from the source of light; hence, if the lamp were *twice* as far from *its* shadow as the candle is from *its* shadow, the lamp would have a candle power of 4. If its distance were three times that of the candle, the lamp's candle power would be 9, and so on.

307. Oxidizing and Reducing Flames. — The flame of a burning hydrocarbon contains both **oxidizing** and **reducing** zones; these have an *excess of hot oxygen*, and of *hot carbon and hydrogen*, respectively. Thus, the Bunsen flame is an *oxidizing flame at its outer edge and tip*. In Fig. 71 (*q. v.*) the lower oxidizing region is designated *L. O.*; the upper region, *U. O.* *Within the flame* the action is chiefly **reduction**. The **best reducing region** is the spot that is still slightly luminous when the holes of the burner are partly opened. Substances are oxidized or reduced in "bead" tests (*cf.* §§ 357 and 399) by being heated *persistently* in the proper region of the Bunsen flame.



FIG. 73.

The Mouth Blowpipe. — Oxidation and reduction tests with solids are often carried out in flames produced by the mouth blowpipe (Fig. 73). The luminous flame, 4 to 5 cm. high, is used. The **assay** (substance to be tested) is placed in a depression hollowed out near one end of a block of charcoal. Air blown into the larger end of the blowpipe comes out at the tip in a small, rapid stream. The tip is held so that the flame produced is inclined about 30° to the horizontal.

The **oxidizing flame** is made by holding the tip of the blowpipe *inside* the luminous flame, one centimeter above the inner cone of unburned gas. The charcoal is held at such a distance, and in such a position, that the assay is in the outer, faintly luminous part of the blowpipe flame.

The **reducing flame** is made by placing the tip just at the outer edge of the middle part of the flame. The assay is held

much nearer the blowpipe than in the oxidizing flame — best, just at the tip of the inner, light-blue cone of the blowpipe flame.

308. Sources of Heat. — The common source of the high temperatures required for heating and manufacturing operations is the combustion of fuels. These consist chiefly of carbon and hydrogen, of hydrocarbons, or of carbon monoxide. In the furnaces used in metallurgy the fuel, the furnace gases, or both, are usually in contact with the ore, or *charge*. Furnaces which avoid this contact are called **muffle furnaces**. In the **reverberatory furnace** (Fig. 86 and § 485) the furnace gases, alone, reach the charge; while in **shaft furnaces**, or kilns, ore and fuel are usually mixed, or in layers (*cf.* Figs. 61, 84, and 88). Many modern kilns, however, avoid this contact (Fig. 84).

Until recently the oxy-hydrogen blowpipe gave the highest temperature attainable by man. Two other sources of very high temperature are now available: (1) **the electric current**, and (2) **thermite**.

The electric current is used in the **electric furnace**, invented by Moissan. Electric furnaces are of two general types:

- (1) Arc furnaces;
- (2) Resistance furnaces.

The *arc furnace* consists of a crucible and covering of refractory materials (Fig. 74). The

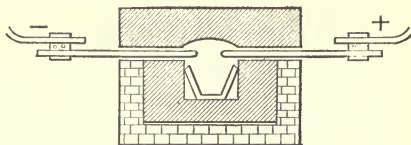


FIG. 74.

charge is heated by the electric arc. In the *resistance furnace*

the high temperature is developed by the passage of the current through the charge itself, or through other materials having a high resistance. The energy of the current is thus changed to heat.

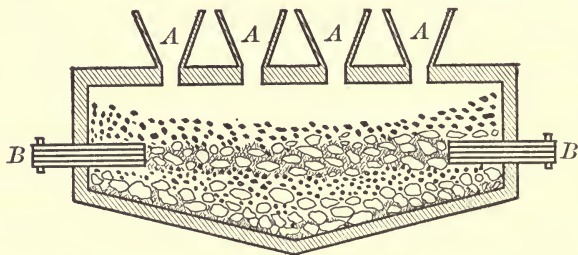
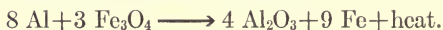


FIG. 75.

Thermite is a mixture of an oxide, such as iron oxide, with aluminum in a proper state of division. The heat set free when aluminum and oxygen unite is enormous, and may be used to give a very high temperature at little cost.



309. Smoke.

The smoke produced in heating and manufacturing has come to be one of the **great nuisances** of civilization. Smoke consists of the gases produced in combustion (CO_2 , CO , H_2O , SO_2 , etc.) and of solid particles of unburned carbon (soot). The carbon thus lost represents actual **waste of fuel**, which could be used in producing heat, if properly burned. But the greatest losses due to smoke are the soiling of streets, vegetation, houses, house-furnishings, and clothing, as well as the injury to the health of persons obliged to breathe smoke-polluted air.

Smoke consumers prevent the escape of unburned carbon by bringing supplies of air into intimate contact with it while it is still hot.

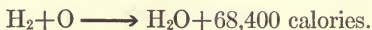
310. Energy Changes Accompany Chemical Changes. — Chemical changes result not only in the formation of new substances, but also in the evolution or the absorption of energy (*cf.* § 27). The energy may appear in the form of heat, light, electric effects, etc.

To illustrate: The union of carbon with oxygen produces carbon dioxide; but at the same time a considerable evolution of heat and light takes place. Since the energy evolved comes from the carbon and the oxygen, carbon dioxide must possess less energy than the elements which produced it. So, also, water has less energy than the hydrogen and oxygen from which it was formed.

A mixture of elements capable of uniting chemically with *evolution* of heat must be looked upon as having **potential energy**. In the act of union this energy is partly given up in the kinetic, i. e., *active*, form; while in the resulting compound there must be *less* energy than existed in the elements. Furthermore, to *decompose* carbon dioxide as much energy must be *added* as was evolved when the elements united.

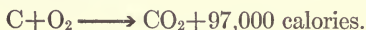
311. Heat of Formation and of Decomposition. — The quantity of heat evolved in many cases of chemical action has been determined (*cf.* **Appendix**, vi). If we call the amount of heat necessary to raise the temperature of one gram of water from 0°

C. to 1° C. a **calorie** we may write the equation for the union of hydrogen and oxygen as follows: —

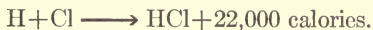


This equation shows not only that 2 grams of hydrogen and 16 grams of oxygen unite to form 18 grams of water, but also that by their union 68,400 calories are liberated.

Similarly, for the union of 12 grams of carbon and 32 grams of oxygen we may write, —



For the union of 1 gram of hydrogen and 35.5 grams of chlorine the equation is, —



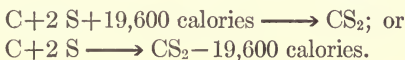
The *difference* between the energy (calculated as heat) possessed by the elements which united to form a compound and that possessed by the compound itself is called the **heat of formation** of the compound.

The **heat of decomposition** of a compound is *numerically equal* to the heat of formation; that is to say, the quantity of heat necessary to separate a compound *into* its elements is just as great as that evolved when the compound was formed *from* its elements.

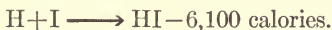
312. Exothermic and Endothermic Reactions. — The heat of formation of water, of carbon dioxide, and of hydrochloric acid is positive (+), heat being

evolved when these compounds are formed; many cases, however, exist in which heat is not evolved, but *absorbed* in the formation of a compound from its elements. In such cases the heat of formation is negative (—).

Thus carbon unites with sulphur (§ 256) with *absorption* of heat. The quantity rendered *potential* is shown in the equation,



Similarly, hydrogen and iodine unite with absorption of heat.



Reactions that proceed with *evolution* of heat are called **exothermic** reactions; while those that take place with *absorption* of heat are called **endothermic** reactions. A substance with a *negative heat of formation* is usually **unstable**. When its decomposition is started, it proceeds *spontaneously*, because energy need not be supplied from the outside. One allotropic form is often unstable because in its change to another form heat is evolved (*cf.* §§ 249 and 345).

It is a general rule, although it has limitations, that *every chemical change that does not require energy from the outside tends to produce those substances which have the greatest heat of formation*. Thus, if a mixture of equivalent weights of gaseous fluorine and chlorine were treated with one equivalent weight of hydrogen, *hydrogen fluoride* would tend to form, because in its formation more heat would be liberated than in the case of hydrogen

chloride. Again, if fluorine were mixed with hydrogen chloride, the reaction would run from left to right, *with liberation of energy*: —



This rule is known as Berthelot's law of maximum work.

313. Heat of Formation Evolved in Stages.

Just as it makes no difference in the total quantity of heat given out whether a given mass of a combustible burns slowly or rapidly (*cf.* § 25), so the total amount of heat evolved (or absorbed) in the formation of a compound is the same whether the compound is formed in one or in several stages.

Thus, the heat of formation of *calcium carbonate*, CaCO_3 , is equal to the sum of the heats of formation of *calcium oxide*, CaO , and of *carbon dioxide*, CO_2 , *plus* the heat evolved when calcium oxide and carbon dioxide unite to form calcium carbonate.

314. Exercises.

1. If cerium and thorium oxides are CeO_2 and ThO_2 , respectively, what are the formulas of the corresponding nitrates? The Welsbach mantle consists, originally, of knitted cotton or silk. This is soaked in a solution of the nitrates of cerium and thorium, dried, and set on fire. Write the equation for the resulting decomposition of the nitrates.

2. Why are the flames of hydrogen and of carbon monoxide non-luminous? Why does kerosene burn with a smoky, luminous flame, while that of gasoline is non-luminous?

3. Account for the differences observed in the burning of anthracite coal, charcoal, and coke, on the one hand, and wood and soft coal, on the other.

4. A standard candle and a Welsbach light were 830 cm. and 6 m., respectively, distant from the shadows cast on the screen of a Rumford photometer (§ 306), when the shadows were

of equal density. What was the candle power of the Welsbach light?

5. A 36-candle power electric light and a standard candle cast shadows of equal density upon the screen of the photometer. What are their relative distances from their respective shadows?

6. Find, in the Table of Heats of Formation (Appendix vi), the values for ethane, ethylene, and acetylene. Which of these three substances is the most stable? The most unstable? Why? Make a similar comparison between water, hydrogen sulphide, and hydrogen iodide.

CHAPTER XXIV.

FLUORINE, BROMINE, IODINE, AND THEIR COMPOUNDS.

315. Halogens. — The elements *fluorine*, *chlorine*, *bromine*, and *iodine* are called “the halogens,” from *hals*, Greek for “salt,” and the suffix *gen*, meaning “a constituent of,” as in “hydrogen,” etc. Their *binary* compounds, *e. g.*, *chlorides*, *bromides*, etc., are called **halides**.

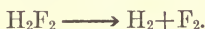
Fluorine and chlorine are gaseous at the ordinary temperature; bromine is a liquid boiling at about 59° C.; while iodine is a black solid which gives off, even at ordinary temperatures, a beautiful, violet vapor.

316. Fluorine. — The element fluorine was known in its compounds long before it was obtained in the *free* condition. The most common of its compounds is *calcium fluoride*, or fluorspar, CaF_2 . Fluorspar derives its name from *fluo*, Latin for “to flow,” and *spar*, meaning “a rock.” The name is applied to this substance owing to the use of fluorspar as a *flux* in metallurgy.

A flux is an easily fusible substance added to the mixture of an ore and a reducing agent to promote *fusion* of the mixture. The substance resulting from the union of the flux with the impurities present is usually called “slag” (*cf.* § 482).

Another important natural fluorine compound is *cryolite*. This is a *double fluoride of aluminum and sodium*; its formula is $\text{AlF}_3 \cdot 3 \text{NaF}$, or Na_3AlF_6 .

Fluorine was prepared by Moissan (1886) by the electrolysis of *anhydrous* hydrogen fluoride containing potassium fluoride, KHF_2 (Fig. 76).



The apparatus may be of copper or platinum, but not of glass (*cf.* § 318).

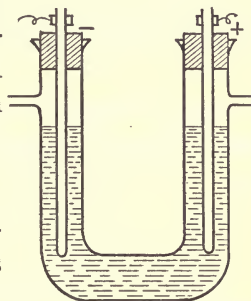
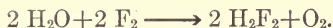


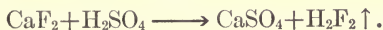
FIG. 76.

317. Properties of Fluorine. — Fluorine is a yellow gas, 1.4 times as heavy as air. It reacts violently with water:



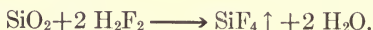
Fluorine unites with hydrogen explosively, *even in the dark* (*cf.* § 118), to form hydrogen fluoride. It does not unite with oxygen (*cf.* § 24). Silicon and antimony form the *fluorides*, SiF_4 , and SbF_3 . Liquid fluorine boils at -187°C . under ordinary pressure.

318. Hydrofluoric Acid. — Hydrogen fluoride is prepared by heating calcium fluoride with concentrated sulphuric acid. The simplest formula (HF) must be *doubled*.

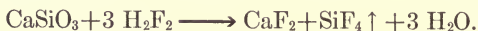


Anhydrous hydrogen fluoride boils at 19° C. The solution is a strong acid. Being *dibasic*, it forms both **acid** and **normal** salts, *e. g.*, KHF_2 and K_2F_2 . Both hydrogen fluoride vapor and its solution are very poisonous. The aqueous solution reacts with almost all the *metals*, forming fluorides and hydrogen, and with their *oxides*, forming fluorides and *water*.

Silicon dioxide (quartz, sand, etc.) and hydrofluoric acid give *silicon fluoride* (a gas) and water.



Glass — a mixture of *silicates* (*cf.* § 394) — reacts with hydrofluoric acid like a mixture of metal oxides and silicon dioxide. With calcium silicate, CaSiO_3 , the equation is, —



Hence, when glass is treated with hydrofluoric acid, the silicon present in the glass *escapes* as SiF_4 , leaving a *depression* in the glass. This fact is made use of in the operation of *etching* glass. The glass is first covered with a thin layer of paraffin, and a design is drawn in the paraffin by means of a sharp point. When the exposed glass is wet with the solution of the acid (a swab of cotton attached to a stick may be used to apply the solution) or is left in the vapor of the acid, the design is *etched* into the glass.

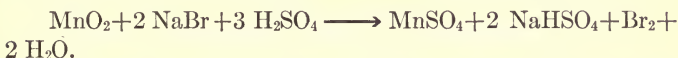
Hydrofluoric acid is commonly kept in bottles of paper, covered inside and out with a thick layer of paraffin. Vessels of lead, platinum, or rubber may also be used.

BROMINE.

319. Preparation of Bromine. — Bromine is found in nature in the *combined* form, chiefly as *bromides*. The most common bromides are those of sodium (NaBr), of potassium (KBr), and of magnesium (MgBr₂).

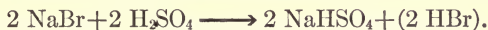
Bromides occur in sea-water and in salt deposits.

Bromine is prepared by heating a bromide with manganese dioxide and dilute sulphuric acid. The bromine vapor evolved is condensed in cold receivers. With sodium bromide the *complete* equation is, —

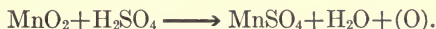


This reaction is like that for the preparation of chlorine (§ 115) from common salt, manganese dioxide, and hydrochloric acid. There are *three* stages: —

(1) Sulphuric acid and sodium bromide give **hydrogen bromide** and sodium hydrogen sulphate.



(2) Sulphuric acid and manganese dioxide give manganous sulphate and **oxygen**.



(3) Hydrogen bromide and oxygen give free **bromine**.



Bromine may also be prepared by conducting the proper amount of *chlorine* into the solution of a bromide. With magnesium bromide the equation is, —



320. Properties of Bromine. — Bromine is a brown liquid about 3.2 times as heavy as water. Its vapor has an odor much like that of chlorine, and affects the eyes. Bromine boils at about 59° C.

The density of bromine vapor shows that the molecule is *diatomic*; its formula is, therefore, Br₂. At about 1000° C. the molecule begins to dissociate into molecules containing only *one* atom each (*cf.* § 142).

Bromine dissolves in water, carbon disulphide, and other solvents. The aqueous solution is called "bromine water."

In the presence of some substance capable of taking up oxygen, bromine reacts with water energetically, according to the equation,



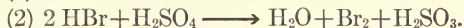
The oxygen is in the *nascent* state (*cf.* § 123). Bromine water is thus a good *oxidizing* agent.

The same action goes on more slowly when no oxidizable substance is present; bromine water thus becomes converted into a dilute solution of hydrobromic acid, HBr.

Bromine is less active than chlorine, but, like chlorine, it unites with hydrogen and with metals. Most bromides are soluble (*cf.* § 130).

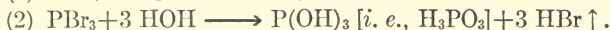
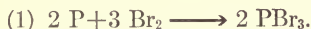
321. Hydrobromic Acid. — Hydrogen bromide cannot be made in a pure state from a bromide and concentrated sulphuric acid, because *some of it is oxidized* by the sulphuric acid. The product is,

therefore, a mixture of *hydrogen bromide*, *bromine*, and *sulphur dioxide* (from the sulphurous acid).



With *dilute* sulphuric acid only reaction (1) takes place.

To prepare pure hydrogen bromide, a mixture of red phosphorus and water is treated with bromine. Phosphorus tribromide is first formed, and is then *hydrolyzed*.



The phosphorous acid is not volatile, while the hydrogen bromide is. To remove bromine vapor, the gas evolved is passed through a U-tube of *moist* red phosphorus.

322. Properties of Hydrobromic Acid. — Hydrogen bromide, like hydrogen chloride, *fumes* in the air, and dissolves readily in water. When distilled, the solution behaves like that of hydrogen chloride: a mixture containing 48% of hydrogen bromide passes over at 126° under 760 mm. pressure. The concentrated aqueous solution has a specific gravity of almost 1.8, and contains 82% by weight of the acid.

Hydrogen bromide begins to *dissociate* into its elements (*cf.* § 73) at about 800° C.; it is, therefore, much less stable than hydrogen chloride, which begins to dissociate at about 1500° C

IODINE.

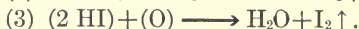
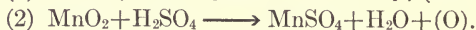
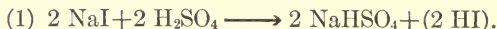
323. Occurrence and Preparation of Iodine. —

The chief source of iodine until recently was the ashes of certain sea-plants which absorb iodine compounds from sea-water. At the present time the element is obtained largely from the Chile saltpeter deposits. In these deposits the iodine is found chiefly as *sodium iodate*, NaIO_3 .

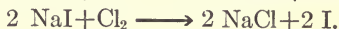
Iodine may be set free from an *iodide* in just the same way that chlorine and bromine are set free from *chlorides* and *bromides* respectively, viz., by heating it with a mixture of manganese dioxide and dilute sulphuric acid. A representative equation is, —



The *stages* of the reaction are:



Iodine may also be set free from an iodide by means of *chlorine* or *bromine* (*cf.* § 319).

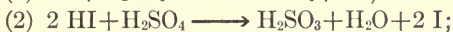


324. Properties of Iodine. — Iodine is, ordinarily, an almost black solid, melting at 114°C . and boiling at about 184°C . Its vapor has a beautiful, violet color; it is about 8.7 times as heavy as air.

Iodine is very soluble in carbon disulphide and in ether, but only slightly soluble in water. It is less active than chlorine or bromine. It stains the skin *brown*, and imparts an intensely *blue* color to starch paste. Iodine *sublimes* (*cf.* § 211) when heated.

Up to above 600° C. the molecule of iodine vapor consists of *two* atoms; above this temperature, *dissociation* takes place. At about 1500° C. only *monatomic* iodine molecules exist.

325. Hydriodic Acid. — Hydrogen iodide is still more unstable than hydrogen bromide. It cannot be made in a pure condition by treating an iodide with concentrated sulphuric acid for the reason that the hydrogen iodide *reduces* the sulphuric acid. The reduction goes not only to *sulphurous acid*, as in the case of hydrogen bromide, but in part even to *hydrogen sulphide*. The equations representing this are, —

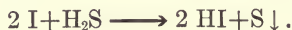


Hydrogen iodide may be made by allowing red phosphorus and iodine to react in the presence of water. Phosphorus tri-iodide is first formed, but is decomposed at once according to the equation,



An aqueous solution of hydriodic acid may best be prepared by making use of a property common to chlorine, bromine, and iodine, *viz.*, the ability of each of these substances to decompose *hydrogen*

sulphide. The sulphur formed, being insoluble, is precipitated; hence the reaction goes on to completion (*cf.* § 253). The equation in the case of iodine is,

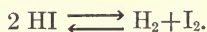


The hydrogen sulphide is conducted into a mixture of iodine and water until the iodine disappears. The sulphur is then filtered off, and the filtrate distilled. After the water has passed off, a heavy liquid is obtained, which boils at 126° C. This is about 57% hydrogen iodide.

326. Properties of Hydriodic Acid. — Hydrogen iodide is about 4.4 times as heavy as air. Like hydrogen chloride and bromide, it is very soluble in water. One cubic centimeter of water at 10° C. and standard pressure dissolves about 450 c.c. of the gas.

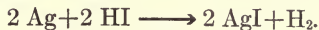
Hydrogen and iodine can be made to unite under appropriate conditions. When uniting they do not *evolve* heat, but *absorb* it. This accounts for the fact that hydrogen iodide is so unstable (*cf.* § 312).

The dissociation of hydrogen iodide is like that of steam (*cf.* § 73). At any temperature above the point at which dissociation begins, the *decomposition* of hydrogen iodide goes on side by side with *recombination* of hydrogen and iodine.



If either product of dissociation is removed from the "sphere of action," the dissociation goes on to completion. Thus, if

silver is placed in hydriodic acid solution, it unites with the iodine as rapidly as iodine is formed. Hence hydrogen is set free.



Because of its ready dissociation, hydriodic acid acts as a powerful *reducing* agent. Oxygen, or any oxidizing agent, gives with it *iodine and water*.



327. Compounds of the Halogens with Oxygen. —

Only three halogen oxides have been actually made; although more — especially one oxide of bromine — are suspected to be capable of existing. The three oxides definitely known are: —

Chlorine monoxide, Cl_2O ;

Chlorine dioxide, ClO_2 or Cl_2O_4 ;

Iodine pentoxide, I_2O_5 .

Chlorine monoxide is an unstable liquid which boils at $+5^\circ \text{ C}$. It explodes with violence giving chlorine and oxygen. It is the anhydride of hypochlorous acid.



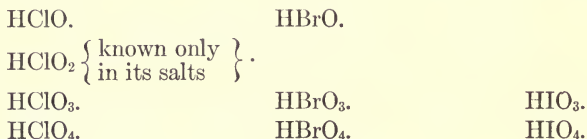
Chlorine dioxide (ClO_2) and *tetroxide* (Cl_2O_4) correspond to the nitrogen oxides NO_2 and N_2O_4 . They are formed with violent explosion when concentrated sulphuric acid acts upon potassium chlorate. Their preparation should not be attempted without *precise directions* and *extraordinary precautions*.

Chlorine dioxide is a reddish-brown liquid, boiling at about 10° C .

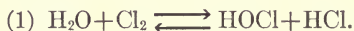
Iodine pentoxide is the only oxide of iodine known at present. It is a white, stable powder; with water it gives iodic acid: it is *iodic anhydride*.



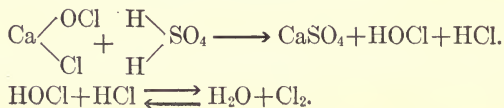
328. Compounds of the Halogens with Oxygen and Hydrogen. — Compounds of the halogens with oxygen and hydrogen are called *oxygen acids*, or *oxy-acids*, of the halogens. They are more numerous than compounds with oxygen alone; for they include at least *three* chlorine acids, *three* bromine acids, and *two* iodine acids. The formulas of these acids are: —



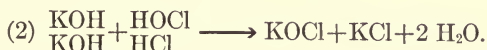
329. Hypochlorous Acid. — When chlorine is dissolved in water, a *small amount* of hypochlorous acid is formed: —



The reverse action (*cf.* § 243) is far more complete than the forward one. This is apparent when the two acids are set free together from bleaching powder. *Chlorine and water* are formed.

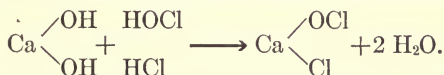


If, however, a **base** is present in the water to which chlorine is added, it unites with the acids as rapidly as they are produced, and the reverse action of (1) does not take place.

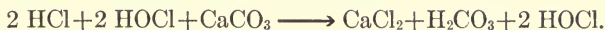


When, therefore, chlorine is passed into a solution of potassium hydroxide, the *stages* of the reaction are shown by (1) and (2). The products in solution are *potassium hypochlorite* and *chloride*.

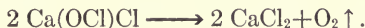
When chlorine is passed into slaked lime, **bleaching powder**, a *mixed salt*, results:—



Hypochlorous acid is a *weak* acid (*cf.* § 178). If chlorine is passed into water containing *suspended* calcium carbonate, the hydrochloric acid formed reacts with the carbonate, but the hypochlorous acid does not. When the solution is distilled, a dilute solution of hypochlorous acid passes over.



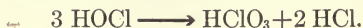
The solution of hypochlorous acid is very **unstable**. In the presence of reducing materials it is a powerful **oxidizing agent**. This accounts for the bleaching properties of chlorine water and of acidified bleaching powder (*cf.* §§ 119, 122, and 123). In the presence of sunlight, chlorine water, *i. e.*, *hypochlorous acid*, gives off oxygen (*cf.* § 119). Bleaching powder also gives oxygen when treated with catalyzers, such as cobalt hydroxide, etc.



Hypochlorous acid is decomposed with **evolution of heat**.

The oxygen liberated thus owes its great activity (**nascent state**) to the excess of energy set free at the same time.

In concentrated solution hypochlorous acid changes spontaneously to *chloric* and hydrochloric acids (*cf.* § 331.)



330. Chlorous Acid, $\text{H}-\text{O}-\text{Cl}=\text{O}$.

Chlorous acid does not exist free. Its potassium salt is produced, in solution, when an aqueous solution of chlorine dioxide, ClO_2 , is treated with potassium hydroxide.

331. Chloric Acid, $\text{H}-\text{O}-\text{Cl} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$. — Chloric acid is

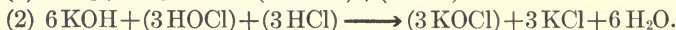
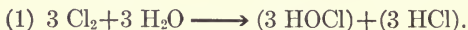
known only in its aqueous solution; this may be concentrated until it contains 40% of chloric acid. Chloric acid is a powerful oxidizing agent.

Chlorates are formed by conducting chlorine into hot, concentrated solutions of alkalies to complete saturation. With potassium hydroxide the *complete* equation is, —



The *chlorate* is separated from the *chloride* by recrystallization from hot water. The chlorate, being much less soluble than the other, separates out first.

Just as hypochlorous acid changes to chloric acid and hydrochloric acid (*cf.* § 329), so solutions of hypochlorites change, when heated, to *chlorates* and *chlorides*. Hence the reaction for the preparation of potassium chlorate has the following stages: —



By adding the factors and products not eliminated, and sub-

tracting the water of (1) from that of (2), we get the *complete equation* given above.

When concentrated acids act upon chlorates, the resulting chloric acid is decomposed with explosive violence (*cf.* § 327). When hydrochloric acid is used, the reaction may be stopped, by dilution with water, before it becomes explosive. The equations are, —



332. Perchloric Acid, $\text{H}-\text{O}-\text{Cl} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{O} \end{smallmatrix}$. — Perchloric

acid is a colorless, explosive liquid about 1.8 times as heavy as water. Its salts, the *perchlorates*, are produced when the chlorates are partly decomposed by heat.

In the decomposition of potassium chlorate (*cf.* § 20), a point is soon reached at which a considerable increase of temperature is needed to continue the evolution of oxygen. The amount of oxygen evolved up to this point is only *one-fifth* of the quantity present in potassium chlorate. If we stop at this stage, we obtain a mixture of *potassium perchlorate* and *potassium chloride*, as shown in the equation, —



The potassium chloride is much more soluble than the perchlorate; hence these substances may be separated by recrystallization from water.

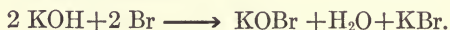
333. Compounds of Bromine with Oxygen and Hydrogen. —

No compounds of bromine and oxygen have been prepared in a pure condition. With

oxygen and hydrogen bromine forms *hypobromous acid*, *bromic acid*, and *perbromic acid*. Bromine reacts with water as chlorine does (*cf.* § 329):

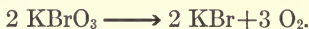


Hypobromites are formed when cold, dilute alkalies are treated with bromine, but with *less* than is required for saturation.



Hypobromites, like hypochlorites, are *oxidizing* agents.

Bromates are formed when *hot* alkalies are **saturated** with bromine (*cf.* chlorates, § 331). Potassium bromate is a white, crystalline solid, like potassium chlorate. Heat decomposes it into potassium bromide and oxygen.



334. Compounds of Iodine with Oxygen and Hydrogen. — Two oxy-acids of iodine are known; they are *iodic* and *periodic* acids.

Iodic acid (HIO_3 or $\text{H}-\text{O}-\text{I} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$) is formed by oxidizing iodine with concentrated nitric acid. It is a crystalline solid. At 170°C . it breaks up into iodine pentoxide (I_2O_5) and water.

Iodates are formed by adding iodine to hot, concentrated solutions of alkalies. With potassium hydroxide the equation is, —



Periodic acid is HIO_4 , or $\text{H}-\text{O}-\text{I} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix} = \text{O}$. Its salts are *per-*

iodates, e. g., sodium periodate, NaIO_4 .

335. The Halogen Family. — From the preceding pages it is evident that there is a great similarity in the properties of the elements *fluorine*, *chlorine*, *bromine*, and *iodine*. The close relation of these elements to one another is yet more marked if we consider that there is a *gradation* in the properties of these elements *in the order of the atomic weights*. Thus, the melting temperatures, the boiling temperatures, and the specific gravities of these elements rise from fluorine (atomic wt. 19) to iodine (atomic wt. 127). The intensity of the color of these elements also increases with the atomic wt: *fluorine* is greenish yellow; *chlorine*, green; *bromine*, brown; and *iodine*, black.

The gradation observed in their *physical* properties is true also of their *chemical* properties. Thus, the elements of *lower* atomic weight can expel those of *higher* atomic weight from their soluble metal salts.

The same gradation of properties is noticed in the *compounds* of the halogens. Thus, the *specific gravity* of the hydrogen compounds *increases* from hydrogen fluoride to the iodide; while the *stability* of these compounds *decreases* in the same order.

In the case of the compounds of the halogens with oxygen, and with oxygen and hydrogen, the order of stability is reversed,

iodine forming the *most* stable ones, chlorine very *unstable* ones, and fluorine none at all.

The same gradation of *color* seen in the elements themselves appears in many of their compounds. Thus, silver chloride is *white*; silver bromide, *light yellow*; silver iodide, *bright yellow*.

Some of the above (and other) facts appear in the following table:—

PROPERTIES.	FLUORINE.	CHLORINE.	BROMINE.	IODINE.
Atomic Weight . . .	19	35.5	80	127
Boiling Temperature.	−187° C.	−33°	+59°	+184°
Specific Gravity . . .	1.15 (liquid)	1.5 (liquid)	3.2 (liquid)	5 (solid)
Union with Hydrogen takes place	In the dark at ordinary temperatures.	In sunlight.	At red heat.	At red heat, but incompletely.
Heat of formation of Hydrogen Compound	37.6 heat units.	22	8	−6.1
Stability of Hydrogen Compound	Most stable.	Decomposed at 1500° C.	Decomposed at 800° C.	Decomposed at 180° C.
Stability of Oxygen Compound	Forms none.	Unstable.	Forms none.	Most stable.

A group of elements related to one another like the halogens is called a “**Natural Family of Elements.**” Several other natural families exist, and will be referred to later.

336. Exercises.

1. How many grams of bromine can be made from 150 grams of potassium bromide by using manganese dioxide and dilute sulphuric acid?

2. How would you separate a mixture of iodine and sand?

3. Could phosphoric acid be used, instead of sulphuric acid, to prepare hydrogen chloride, bromide, and iodide? Write the possible equations. Has it any advantages over sulphuric acid? What are its disadvantages? Name *three* properties an acid **must** have to be usable in setting volatile acids free from their salts.

4. How could you distinguish, by chemical means, between a chloride, a bromide, and an iodide?

5. How could you identify a fluoride, *e. g.*, calcium fluoride?

6. Why is potassium fluoride added to anhydrous hydrogen fluoride in the preparation of fluorine by electrolysis?

7. Write the equations for the action of bromine water upon sulphurous acid; upon hydrogen sulphide; upon iron.

8. What would you use to dry hydrogen bromide and iodide?

9. Give the meaning of the names of the halogens.

10. Write the equation for the preparation of iodic acid.

11. Give the equations for **all the stages** of the reaction by which potassium iodate is prepared. What additional reaction is necessary to prepare the iodide from the iodate?

12. Write the equations for the action of potassium hydroxide upon chlorine dioxide. Upon chlorine monoxide.

13. What is the anhydride of perchloric acid?

14. A certain compound has the following composition: C, 12.77%; H, 2.12%; Br, 85.11%. At 137° C. and 760 mm. 188 c.c. of its vapor weigh 1.06 g. Find its formula.

CHAPTER XXV.

OZONE AND HYDROGEN PEROXIDE.

337. Ozone. — Oxygen which has been exposed to the silent electric discharge possesses *new* properties. It has a peculiar odor and oxidizing powers not possessed by ordinary oxygen. Thus, it oxidizes silver and mercury *at once*, whereas these metals are not acted upon by oxygen at ordinary temperatures.

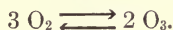
These new properties are due to the presence in the oxygen of another substance, called **ozone**. The name *ozone* is from the Greek *ozein*, to smell.

The same substance is produced in almost every case of oxidation. An illustration of this is the slow oxidation of phosphorus. If moist phosphorus is placed in a covered vessel, the peculiar odor of ozone soon appears. Ozone is formed, also, in the electrolysis of water, and appears at the + electrode along with oxygen.

When ozone is examined, it is found to contain nothing but oxygen; it is, in fact, an *allotropic form of oxygen* (cf. § 249). When oxygen changes into ozone there is a *contraction* of volume amounting to one-third of the volume of oxygen taken. Ozone is, therefore, one and one-half times as heavy as oxygen. Its molecular weight is 48 instead of 32;

hence the molecule of ozone contains *three* oxygen atoms, and is written O_3 .

The relation of ozone to oxygen is one of equilibrium: —



The forward change is accompanied by *absorption* of heat; hence, the *instability* of ozone. In the reverse change, the energy reappears, giving **nascent** oxygen.

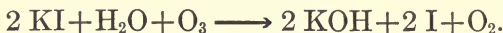
338. Properties of Ozone. — As might be expected, the *oxidizing* power of ozone is very great. Moist phosphorus and sulphur are converted by it into phosphoric and sulphuric acids, respectively; and ammonia is at once oxidized to nitric acid. Organic coloring substances, *e. g.*, indigo and litmus, are at once decolorized by ozone. The bleaching of fabrics on exposure to the air is probably due to the action of ozone present in the air.

When ozone is heated, its molecule is decomposed, and ordinary oxygen results. The reversion of ozone to oxygen is accompanied by an *expansion* of volume just equal to the contraction that takes place when oxygen changes into ozone.

Ozone is readily absorbed by oil of turpentine; hence, the amount of ozone formed in a given volume of oxygen may be determined by exposing the *ozonized* oxygen to this substance. Only about *six per cent* of a given amount of oxygen can be converted into ozone, because the reverse change of ozone into oxygen soon produces a condition of equilibrium.

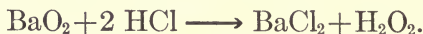
The presence of ozone in ozonized air is readily detected by means of a mixture of potassium iodide

and starch paste — best upon a piece of filter paper. The ozone sets iodine free, probably according to the equation,

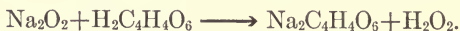


339. Hydrogen Peroxide. — Closely related to ozone, and long confused with it, is *hydrogen peroxide*, H_2O_2 . Hydrogen peroxide is a colorless liquid about one and one-half times as heavy as water; it possesses remarkable oxidizing and reducing powers.

A dilute solution of hydrogen peroxide may be made by adding *barium peroxide*, BaO_2 , to dilute hydrochloric acid. The equation is, —



A somewhat better way is to treat a dilute solution of tartaric acid with sodium peroxide, Na_2O_2 .



Sodium peroxide is made by heating sodium to about 350°C . in air free from carbon dioxide.

When phosphorus is partly immersed in water, it acts upon the moist air to form both hydrogen peroxide and ozone. Both of these substances are formed, also, by holding a hydrogen flame against a piece of ice.

Hydrogen peroxide is formed in the electrolysis of water, if oxygen is passed into the water at the negative (—) electrode. The oxygen is reduced by the nascent hydrogen evolved at the electrode,

Hydrogen peroxide is found in the air, and in all rain water and snow.

340. Properties of Hydrogen Peroxide. — Hydrogen peroxide may be obtained almost pure by distilling a dilute aqueous solution of it at low pressure. The apparatus for distilling at reduced pressure is essentially as shown in Fig. 77.

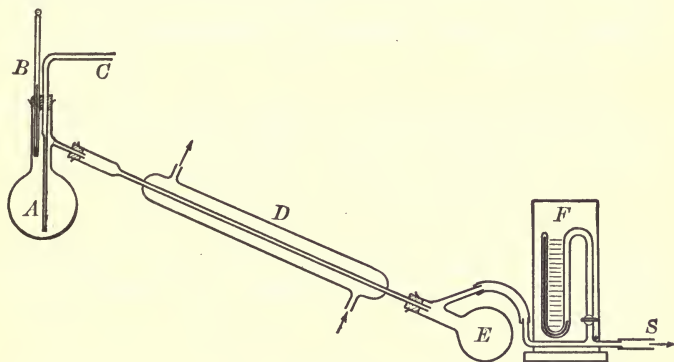


FIG. 77.

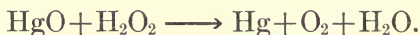
A distilling flask (A) is provided with a thermometer (B) and a capillary³ tube (C). The capillary tube allows a very small stream of air to be drawn through the apparatus. The distilling flask is connected *air-tight* with the condenser (D) and the receiver (E). The pressure, in millimeters of mercury, is indicated by the *manometer* (F). The air is exhausted at S by a water or mercury suction-pump.

At 26 mm. pressure hydrogen peroxide boils at 69° C.; under the same pressure water boils at 27° C.; hence the two substances can be separated

readily. The aqueous solution of hydrogen peroxide has a bitter taste and produces white spots upon the skin. It is a powerful antiseptic.

Hydrogen peroxide decomposes readily, especially in the presence of *basic* substances. The products are water, and oxygen in the nascent condition; hence hydrogen peroxide is a powerful oxidizing agent. It decolorizes indigo, litmus, etc., as ozone does. It at once oxidizes hydrochloric acid to water and chlorine.

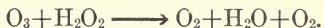
Hydrogen peroxide acts also as a *reducing* agent *with evolution of oxygen*. Thus, it reduces mercuric oxide to mercury and sets oxygen free.



One atom of each oxygen molecule (O_2) comes from the hydrogen peroxide, and the other from the oxide reduced.

Potassium permanganate solution is at once decolorized by hydrogen peroxide, and potassium chromate and bichromate solutions are changed to a green color. All of these are *reductions*.

Ozone and hydrogen peroxide *reduce* each other.



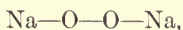
Hydrogen peroxide, like ozone, decomposes with *evolution* of heat; this accounts for its instability and oxidizing power.

The *common test* for the presence of hydrogen peroxide in a solution is to add to the solution in a test tube about two or three cubic centimeters of ether, and then *one drop* of potassium bichromate

solution. When the test tube is shaken, the layer of ether is colored a beautiful blue, if hydrogen peroxide is present.

341. Composition of Hydrogen Peroxide. — Hydrogen peroxide is composed of 1.01 parts, by weight, of hydrogen to every 16 parts of oxygen. Its molecular weight is 34; hence its formula is H_2O_2 . The constitutional formula of hydrogen peroxide is $\text{H}-\text{O}-\text{O}-\text{H}$.

The effect of the *structure* of the molecule, *i. e.*, the way in which the atoms are united, upon the properties of substances, is admirably illustrated by the differences in the behavior of the two classes of *dioxides*. Thus, while *calcium peroxide* (CaO_2), *sodium peroxide* (Na_2O_2), and *barium peroxide* (BaO_2) give hydrogen peroxide when treated with dilute acids, *lead dioxide* (PbO_2) and *manganese dioxide* (MnO_2) do not. The structure of all *true* peroxides is like that of hydrogen peroxide. The constitutional formula of sodium peroxide, is, therefore,



and that of barium peroxide, $\text{O}-\text{O}$. The graphic formula of



the *dioxides* is different, that of *manganese dioxide* being, probably, $\text{Mn} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$, and that of *lead dioxide* $\text{Pb} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$.

342. Exercises.

1. How much heat is evolved when a gram-molecular weight of hydrogen peroxide gives a g. m. wt. of water (*cf.* Appendix vi)?

2. If oxygen is *bivalent*, write the constitutional formula of ozone.

3. Name all the substances studied up to the present that are bleaching or disinfecting agents. Are any *not* sources of nascent oxygen?

4. When 10 g. of a certain solution of hydrogen peroxide are treated with acidified potassium permanganate solution, each drop of the permanganate is decolorized, until 0.15 g. available oxygen has been added. What is the % of H_2O_2 in the solution?

CHAPTER XXVI.

THE NITROGEN FAMILY.

PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH.

A. Phosphorus.

343. Occurrence and Preparation of Phosphorus. — Phosphorus is found in nature only in the combined form, chiefly in *phosphates*. The most abundant phosphate is calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. Calcium phosphate exists in the soil, and is taken up from it by plants. Animals consume phosphates in their food.

Phosphorus is made from *bone-ash*, which is 60% to 70% $\text{Ca}_3(\text{PO}_4)_2$, or from natural phosphates. The phosphate is heated with *charcoal* and *sand* in an electric furnace (Fig. 78).

The charge is fed into a hopper, *C*, with trap bottoms, *E* and *F*, to prevent the escape of phosphorus while the charge is being put in. The conveyor, *G*, forces the charge into the furnace.

The heat for the reaction is developed by the resistance which the current encounters between the electrodes, *A* and *B*. The

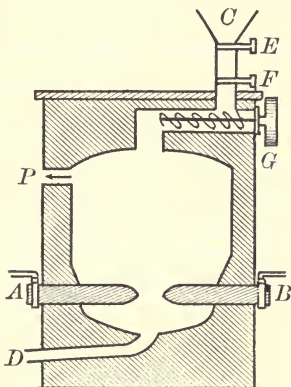
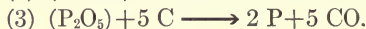
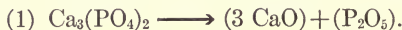


FIG. 78.

slag is drawn off through *D*. Phosphorus vapor escapes through *P*, and is condensed under water. Crude phosphorus is purified by redistillation. It is then pressed, while liquid (under water), through a bone-ash filter. The phosphorus thus obtained is a white, transparent solid. About 3,000 tons are made annually.

The *partial equations* for the reaction are, —



Hence the **complete equation** is, —



344. Properties. — Phosphorus, like *sulphur*, exists in several allotropic forms. Ordinary or *yellow* phosphorus has a specific gravity of about 1.8, melts at about 45° C., and boils at 287° C. It is insoluble in water, but dissolves readily in *carbon disulphide*, CS₂. It is very *poisonous*.

Phosphorus derives its name, which means “bearer of light” (*cf.* Latin, *lucifer*), from its property of *phosphorescing*, i. e., glowing in the dark. This phenomenon is caused by slow combustion on the surface of the phosphorus.

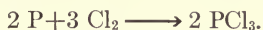
Ordinary phosphorus ignites in air at 40° C., and burns with a hot flame to phosphorus *trioxide* and *pentoxide*.



The spontaneous ignition of finely divided phosphorus has already been described (*cf.* § 31).

Phosphorus unites readily with chlorine, bromine, and iodine even at the ordinary temperature. Two compounds of phosphorus and chlorine are possible, viz., the *trichloride*, PCl₃, and

the *pentachloride*, PCl_5 . Phosphorus trichloride is a liquid; phosphorus pentachloride, a crystalline solid.



345. Red Phosphorus. — A great difference exists between yellow phosphorus and the *red* modification. Red phosphorus is a reddish powder 2.2 times as heavy as water, infusible at red heat, unable to phosphoresce, insoluble in carbon disulphide, and not poisonous. It ignites at about 260° C. in air. Red phosphorus unites with the halogens only when heated.

Red phosphorus is prepared by heating the ordinary form in closed iron tubes to 300° C. A small amount of the yellow phosphorus remains unchanged; this is removed by means of carbon disulphide, in which the red variety is insoluble.

When a given amount of red phosphorus is burned, there is much less heat liberated than with an equal amount of the *yellow* form; the red has therefore much less energy than the yellow. This statement agrees with the known fact that when yellow phosphorus is changed into the red there is an *evolution* of heat.

346. Molecular Weight of Phosphorus. — The weight of a liter of phosphorus vapor is almost four times that of a liter of oxygen at the same temperature and pressure; consequently the molecular

-weight of phosphorus, as a vapor, must be about 124, that is, about four times the atomic weight. The molecular formula of phosphorus vapor is thus written P_4 , just as that of oxygen is O_2 .

347. Matches. — Most of the phosphorus that is made is used to *tip* matches. The ordinary friction match, as made at present, consists of a splint of wood tipped, *first*, with sulphur, and *then* with a mixture containing some oxidizing agent, phosphorus, and an adhesive substance, like glue. The oxidizing agent may be *potassium nitrate* or *chlorate*, or the oxide of lead known as *red lead*, which has the formula Pb_3O_4 .

The chemical operations involved in lighting a match are essentially as follows: —

(1) The heat generated by rubbing the tip of the match against a rough surface causes the phosphorus to combine with the oxygen of the oxidizing agent in immediate contact with it.

(2) The combustion of the phosphorus causes the sulphur to be raised to the kindling temperature of sulphur.

(3) The burning of the sulphur raises the temperature of the wood to the kindling point; *and the match burns.*

Safety matches have not the property of being easily ignited when rubbed; they require contact with a specially prepared surface. This surface is usually on the side of the match box, and consists of red phosphorus mixed with sand. The *tip* of the safety match generally contains antimony trisulphide (Sb_2S_3), an oxidizing agent, and glue.

348. Hydrogen Phosphide (PH_3). — Hydrogen phosphide, or *phosphine*, is a colorless gas which, as ordinarily made, is *spontaneously combustible*. The *common method* of preparing it is to heat a mixture of yellow phosphorus and a concentrated solution of *sodium hydroxide*. The equation is, —

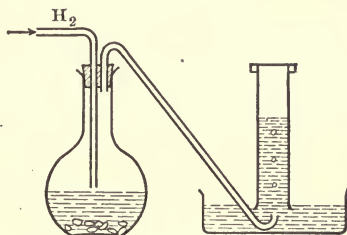
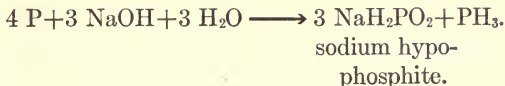
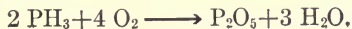


FIG. 79.

The apparatus (Fig. 79) consists of a generating flask containing the phosphorus and the sodium hydroxide solution. The stopper of the flask has two holes, one for a tube from a hydrogen generator and the other for a delivery tube ending under water. The air of the apparatus is first washed out by means of hydrogen (or illuminating gas); the gas then cut off, and the flask is heated. The escaping phosphine may be collected in a receiver, as shown in the figure, and this exposed to the air, or the bubbles of the gas may be allowed to escape through the water directly into the air. The material of the white smoke formed when phosphine burns is *phosphorus pentoxide*, *water*, and *phosphoric acid*.

The equation for the combustion of phosphine is,—

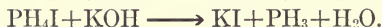
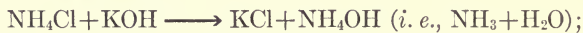


Pure phosphine is not actually ignited until its temperature reaches 100°C . As the gas is ordinarily prepared, however, it contains small amounts of the vapor of another phosphide of hydrogen (P_2H_4), which is spontaneously combustible, and which, therefore, ignites the phosphine.

349. Phosponium Salts. — Phosphine may be regarded as *ammonia*, NH_3 , with its nitrogen replaced by phosphorus. Although similar to ammonia in composition, phosphine is much less *basic*. The aqueous solution of phosphine is not alkaline at all; the compound PH_4OH can hardly be present in the solution.

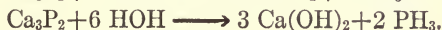
Phosphine can, however, be made to unite with the *halogen acids*. The compounds thus formed correspond with the *ammonium* salts of the halogens; hence, they are called *phosponium* salts. *Phosponium bromide* (PH_4Br) and *phosponium iodide* (PH_4I) are much like *ammonium* bromide and iodide, respectively.

Phosponium iodide is decomposed by soluble hydroxides, much as ammonium chloride is (*cf.* § 203). This fact is evident from the equations, —



350. Phosphides. — The phosphides of the metals may be considered derivatives of *hydrogen phosphide*, just as *sulphides* are of *hydrogen sulphide*. The formula of *calcium phosphide* is Ca_3P_2 ; of *silver phosphide*, Ag_3P .

Calcium phosphide is a white solid; when it is treated with water or with hydrochloric acid, it gives off hydrogen phosphide. The equation resembles that for the action of hydrochloric acid upon ferrous sulphide (*cf.* § 253).



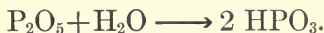
351. Oxides of Phosphorus. — Two common oxides of phosphorus are known, viz., the *trioxide* (P_2O_3) and the *pentoxide* (P_2O_5). Both are white solids.

The weight of a given volume of phosphorus trioxide in the gaseous state is known to be *twice* that demanded by the formula P_2O_3 ; consequently it is better to write the formula P_4O_6 .

Phosphorus pentoxide is formed when phosphorus burns in air or oxygen *free from moisture*.



It is a bulky, white solid which has great attraction for moisture; when put into water it hisses like hot iron. The first product is *metaphosphoric acid*, HPO_3 .



Phosphorus pentoxide has been referred to as capable of decomposing anhydrous nitric acid and producing *nitrogen pentoxide* (*cf.* § 233). It is the *anhydride* of metaphosphoric acid, as nitrogen pentoxide is of nitric acid.

352. Oxygen Acids of Phosphorus. — Several compounds of phosphorus with oxygen and hydrogen are known. Three of these form a series like the

oxygen acids of chlorine (*cf.* §§ 168 and 328); they are, —

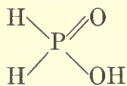
Hypophosphorous acid, H_3PO_2 ;

Phosphorous acid, H_3PO_3 ;

Phosphoric acid, H_3PO_4 .

353. Hypophosphorous Acid. — Attention has already been called to the fact that when phosphorus acts upon sodium hydroxide (*cf.* § 348) it produces *sodium hypophosphite* (NaH_2PO_2) as well as phosphine. With barium hydroxide, *barium hypophosphite*, $\text{Ba}(\text{H}_2\text{PO}_2)_2$, is produced.

The hypophosphites are salts of hypophosphorous acid. This is a *monobasic* acid (*cf.* § 166). Its constitutional formula is

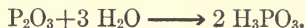


, only the hydrogen atom attached to oxygen being replaceable by metals.

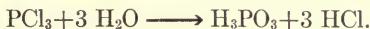
Hypophosphorous acid is a powerful *reducing agent*, owing to the ease with which it goes over into phosphoric acid.



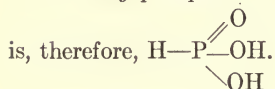
354. Phosphorous Acid. — Phosphorous acid is an intermediate product in the oxidation of hypophosphorous acid. It is itself a reducing agent, owing to its ready oxidation to phosphoric acid. Its *anhydride* is phosphorus trioxide, P_2O_3 .



Phosphorous acid may be prepared by treating *phosphorus trichloride* or *tribromide* with water (cf. § 321).

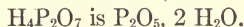
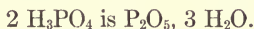


Ordinary phosphorous acid is *dibasic*; its structural formula



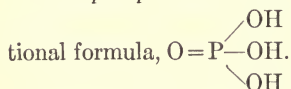
355. The Phosphoric Acids. — The three phosphoric acids are, (1) *orthophosphoric acid*, or simply *phosphoric acid* (H_3PO_4); (2) *pyrophosphoric acid* ($\text{H}_4\text{P}_2\text{O}_7$), and (3) *metaphosphoric acid* (HPO_3).

The anhydride of all three phosphoric acids is P_2O_5 : —



Evidently, the molecule $\text{H}_4\text{P}_2\text{O}_7$ is **two** molecules of H_3PO_4 minus *one* H_2O , and that of HPO_3 is **one** of H_3PO_4 minus **one** of H_2O .

Orthophosphoric acid is *tribasic*, as indicated by the constitu-



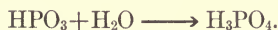
356. Preparation of the Phosphoric Acids. — The best way to obtain *orthophosphoric acid* is to treat red phosphorus with nitric acid, and to evaporate the resulting solution. At the ordinary temperature the acid consists of colorless, deliquescent crystals.

Pyrophosphoric acid is best made by heating the *ortho*-acid for some time to 260° C.; the *meta*- acid is made by heating the *ortho*- or the *pyro*- acid to 300° C.

Metaphosphoric acid always results when phosphorus pent-oxide dissolves in water.



When the *meta*- acid is boiled with water it goes over into the *ortho*- acid.

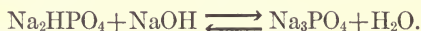


357. Phosphates. — Phosphoric acid forms two *acid* salts and a *normal* salt (*cf.* § 164): —

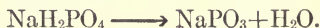
- (1) NaH_2PO_4 is sodium di-hydrogen phosphate.
- (2) Na_2HPO_4 is di-sodium hydrogen phosphate.
- (3) Na_3PO_4 is tri-sodium phosphate.

Salts like the *first*, in which one-third of the hydrogen is replaced, are called *primary* phosphates; those like the second are *secondary* phosphates. The normal salts are *tertiary* phosphates. The corresponding *calcium* salts have the formulas $\text{Ca}(\text{H}_2\text{PO}_4)_2$, CaHPO_4 , and $\text{Ca}_3(\text{PO}_4)_2$, respectively.

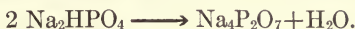
The common *sodium phosphate* of the laboratory is Na_2HPO_4 . It is slightly *alkaline* to litmus (*cf.* § 184). The “acid” sodium phosphate is NaH_2PO_4 . Normal sodium phosphate is obtained by evaporating a solution containing the ordinary phosphate and sodium hydroxide. In solution it is hydrolyzed: —



When a **primary** phosphate is heated, a *metaphosphate* results:

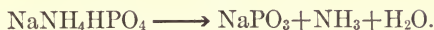


A **secondary** phosphate gives a pyrophosphate when heated:



A **tertiary** phosphate is not decomposed by heating.

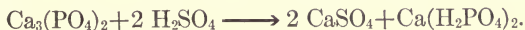
The so-called "*metaphosphate bead*" is made by heating either sodium di-hydrogen phosphate or sodium ammonium hydrogen phosphate upon a loop of platinum wire. Sodium ammonium hydrogen phosphate (also called "*microcosmic salt*") has the formula $\text{NaNH}_4\text{HPO}_4$. When heated it first loses ammonia, like any ammonium salt of a "*fixed*" acid, giving sodium di-hydrogen phosphate. This then loses water.



Sodium metaphosphate reacts with the oxides of metals, forming *mixed* orthophosphates. Some of these have characteristic colors, and are used as **tests** for the metals.



358. Uses of the Phosphates. — The phosphate found in bone-ash and in phosphate rocks is *normal* calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. This is insoluble in water. To convert it into soluble form for the use of plants it is treated with sulphuric acid. This changes it into the *primary* phosphate, which is soluble.



The primary phosphate is commonly known as "soluble phosphate"; the mixture of the primary salt and calcium sulphate is called "superphosphate." The primary phosphate is also used in "acid phosphate" baking powders (*cf.* § 280).

Prospates Necessary for Plants. — To be fertile, soil must contain calcium phosphate, an essential plant food. When the crops are removed, part of the phosphate of that region goes

with them; hence, phosphate must be returned to the soil if the land is to yield good harvests. If the crops are used as food for animals, part of the phosphate returns to the soil in manure; if not, other fertilizers must be used. Nature usually keeps a soil fertile by means of decaying vegetation, which forms with the soil "vegetable mould."

Fertilizers. — A *complete* fertilizer supplies *potassium*, *nitrogen*, and *phosphorus*. Most fertilizers, however, contain only one or two of these essentials.

Potassium is usually returned to the soil as the *sulphate* or *carbonate* (wood-ashes; cf. § 420); sometimes as *chloride*.

Nitrogen is frequently supplied as *ammonium salts*, or as *nitrates*, especially *sodium nitrate* (cf. § 418). Nitrogen is also contained in *guano*.

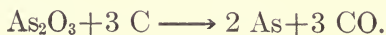
Phosphorus is contained in fertilizers chiefly as "soluble phosphate," which is obtained by treating phosphate rocks or bone-ash with sulphuric acid.

The dry residue left after the *waste products* of slaughter-houses, *e. g.*, tainted meat, bones, hoofs, etc., are deprived of fat, oil, and gelatine, makes a good fertilizer. The fat is used as soap-stock.

B. Arsenic.

359. Occurrence and Preparation of Arsenic. — The element arsenic is found in nature both free and combined. Its chief ores are *realgar* and *orpiment* (As_2S_2 and As_2S_3 , respectively), the *oxide* (As_2O_3), and *arsenopyrite* (FeAsS). Arsenopyrite is iron pyrites (FeS_2) with half of the sulphur replaced by arsenic.

The element may be prepared by reducing the oxide with charcoal.

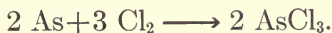


360. Properties of Arsenic. — Arsenic forms compounds which correspond closely with the compounds of phosphorus. The element itself is, however, more metallic than phosphorus. It exists in at least *two* allotropic forms.

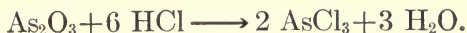
The ordinary form of arsenic is gray, has a crystalline structure, and is about 5.7 times as heavy as water. It is not at all malleable, but, on the contrary, crumbles to powder when struck.

When arsenic is heated to about 500° C. out of contact with the air, it *sublimes*, forming a yellow vapor. By comparing the weight of a known volume of this vapor with that of oxygen under the same conditions, it is found that the molecular weight of arsenic is about 300. The atomic weight being 75, the molecule must contain *four* atoms; hence, the molecular formula is As₄. Above 1700° C., however, most of the molecules containing four atoms *dissociate* into simpler molecules of *two* atoms each, *i. e.*, As₂ molecules.

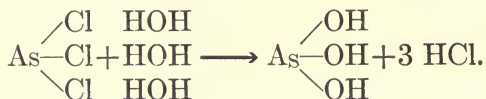
Arsenic begins to burn at about 180° C. to form arsenic trioxide, As₂O₃. The flame is bluish-white. Like phosphorus and antimony, arsenic unites with chlorine at the ordinary temperature to form the chloride, AsCl₃.



The same substance is formed when arsenic trioxide, As₂O₃, is treated with concentrated hydrochloric acid solution.



Arsenic trichloride is a colorless liquid; it is decomposed by an *excess* of water, giving *arsenious acid* and hydrochloric acid.



Arsenic trichloride is thus like *phosphorus* trichloride, which with water gives phosphorous acid and hydrochloric acid (*cf.* § 354).

361. Hydrogen Arsenide. — Arsenic combines with nascent hydrogen to form *hydrogen arsenide* or *arsine*, AsH_3 , a substance which corresponds with phosphine gas, PH_3 . Arsine cannot, however, be made to unite with hydrobromic acid, etc., to give compounds resembling ammonium and phosphonium salts (*cf.* § 349).

The most common method of getting arsine (mixed with hydrogen) is to add an arsenic compound to a flask in which hydrogen is being generated; the nascent hydrogen unites with the arsenic of the compound.

Marsh's Test. — Advantage is taken of the properties of arsine to test for the presence of arsenic in any substance; the test is known as *Marsh's test*.

To a flask in which pure hydrogen is being generated (Fig. 80), there is attached a calcium chloride tube and a hard glass tube drawn out as shown in the figure. The hydrogen is allowed to pass off until the usual test (*cf.* § 50) shows that all air has

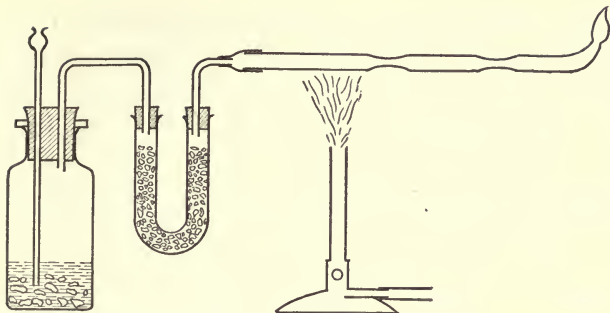


FIG. 80.

been removed. The jet of hydrogen is now lighted, and a few drops of the liquid to be tested for arsenic are added through the thistle-tube. If arsenic is present, the flame changes to a bluish-white color, and a cold piece of porcelain held in the flame receives a shiny, black deposit, called an "arsenic mirror."

If the hard glass tube is heated, the arsine passing through it is decomposed, and an arsenic mirror appears in the tube. Here the arsenic may be identified by passing hydrogen sulphide, H_2S , through the heated tube. The same precautions must be taken to have all air removed as in the case of hydrogen. Hydrogen sulphide changes the arsenic into *arsenic trisulphide*, As_2S_3 ; this is a golden-yellow solid called *orpiment* (from *auri pigmentum*). If, now, dry hydrochloric acid gas is passed through the tube, the arsenic trisulphide does not change. These properties serve to distinguish between the arsenic mirror and that of *antimony* (cf. § 369).

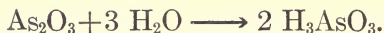
362. Arsenic Trioxide. — The oxides of arsenic are the *trioxide* (As_2O_3) and the *pentoxide* (As_2O_5); these correspond to the phosphorus oxides. Arsenic trioxide (often called "arsenic" or "white arsenic")

is the most common arsenic compound. It is a white powder which sublimes, without melting, at about 220° C. The vapor has a garlic odor. When the vapor solidifies, the arsenic trioxide appears in the form of a transparent mass. At very high temperatures the molecule of the vapor is represented by As_2O_3 ; but between 220° and 700° C. the molecules are *doubled*, and the formula is As_4O_6 .

Uses. — Arsenic trioxide is used in medicine and as a poison. Its poisonous action upon the human system is rather slow, because it dissolves only slowly in the liquid of the stomach. The antidote is a mixture of ferric hydroxide $[\text{Fe}(\text{OH})_3]$ and magnesia (MgO).

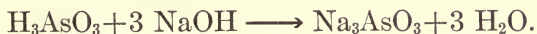
The people of certain mountain districts are addicted to the use of arsenic trioxide because it enables them to breathe more easily when climbing. By beginning with very small quantities and gradually increasing the dose, they are able to take much more than the lethal dose without injury. But the difficulty comes when they try to leave off the habit; for they then suffer all the effects of arsenic poisoning.

363. Arsenious Acid. — Arsenic trioxide is slightly soluble in water; the solution probably contains *arsenious acid*, H_3AsO_3 .

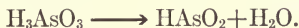


Arsenious acid is not known in the free state because it breaks up into arsenic trioxide (its anhydride) and water. The salts of arsenious acid are called *arsen-*

ites. Solutions of these are formed when arsenic trioxide is treated with alkalis. Thus, sodium hydroxide and arsenic trioxide (with water this is *arsenious acid*) form *sodium arsenite*, Na_3AsO_3 .

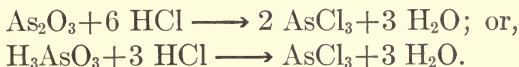


Many arsenites are derived from *metarsenious acid*, HAsO_2 , which may be looked upon as arsenious acid *minus* water.



Sodium metarsenite would be NaAsO_2 .

Double Nature of Arsenious Acid. — Arsenic trioxide (or arsenious acid) reacts not only with alkalis, giving arsenites and water, but also with acids, giving *arsenic salts* and water. Thus, with concentrated hydrochloric acid and arsenic trioxide, we get arsenic trichloride and water.

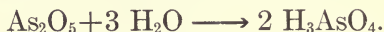


Arsenious acid has thus a *double* nature; for toward strong bases it acts like an acid, forming with the base an *arsenite*; while toward a strong acid it acts like a base, giving with the acid a *salt* and water. Arsenic is, in fact, *intermediate* between the non-metals and the metals.

Arsenic Greens. — At least two arsenic compounds have a bright green color; these are *copper arsenite*, called “Scheele’s green,” and a mixture of copper arsenite and copper acetate, called “Schweinfurt’s green.” Both of these are sold as “Paris

green." These dyes were formerly used to color wall-paper, paints, etc. They are too dangerous, however, and are now rarely used as dyes. Paris green is used to destroy potato-bugs, etc.

364. Arsenic Acid. — Arsenic pentoxide, As_2O_5 , is the anhydride of *arsenic acid*, H_3AsO_4 .



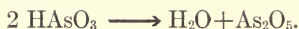
Arsenic acid is formed by dissolving arsenic or arsenic trioxide in concentrated nitric acid. (Compare the preparation of phosphoric acid from phosphorus, § 356.) The arsenic acids have formulas of the same type as those of phosphorus: —

H_3AsO_4 is orthoarsenic acid;

$\text{H}_4\text{As}_2\text{O}_7$ is pyroarsenic acid;

HAsO_3 is metarsenic acid.

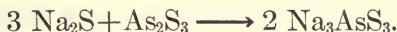
Metarsenic acid finally gives, by loss of water, arsenic pentoxide.



The *arsenates* are like the corresponding phosphates.

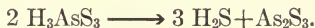
365. Arsenic Trisulphide. — When the solution of an arsenic compound is treated with hydrogen sulphide, a yellow precipitate is generally produced; this consists of either the trisulphide (As_2S_3) or the pentasulphide (As_2S_5). Both sulphides react with ammonium sulphide $[(\text{NH}_4)_2\text{S}]$ and other soluble sulphides. The solution contains a *sulpharsenite*

or *sulpharsenate*. Thus with sodium sulphide and arsenic trisulphide the equation is, —



The sulpharsenite (Na_3AsS_3) is simply an arsenite with its *oxygen* replaced by *sulphur*.

When the sulpharsenite is treated with a dilute acid, *e. g.*, hydrochloric acid, *sulpharsenious acid*, H_3AsS_3 , is set free; this breaks up into hydrogen sulphide and arsenic trisulphide. Arsenic trisulphide, being insoluble, is reprecipitated. These facts are shown in the equations, —

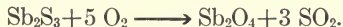
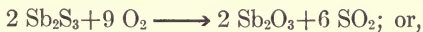


Ammonium sulpharsenite, $(\text{NH}_4)_3\text{AsS}_3$, undergoes a similar decomposition.

C. Antimony.

366. Preparation of Antimony. — Antimony is found in nature chiefly combined with sulphur in the mineral *stibnite*, Sb_2S_3 . To obtain the element the sulphide is first *roasted*, i. e., heated in a stream of air, and then heated with charcoal.

Roasting converts the antimony sulphide into the *trioxide* (Sb_2O_3), or the *tetroxide* (Sb_2O_4), and sulphur dioxide.



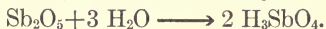
The reduction of either of these oxides by charcoal gives antimony and carbon monoxide.



367. Physical Properties. — Antimony is a solid having a bright, silvery luster which is not easily tarnished in air. Antimony is not malleable. At about 430° C. it melts to a liquid of a slightly higher specific gravity. When melted antimony solidifies it *expands* again; hence antimony is valuable as a constituent of materials for *casts*, such as type-metal. The specific gravity of the solid is 6.7. The specific gravity of the vapor shows that in the *gaseous* condition the formula of the molecule is Sb_2 (*cf.* §§ 346 and 360).

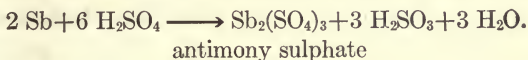
368. Chemical Properties. — Antimony burns in the air to form the trioxide or the tetroxide. It combines with chlorine to give antimony *trichloride* (*cf.* § 118) or the *pentachloride*, SbCl_5 . With fluorine, bromine, and iodine it forms similar compounds.

Antimony is insoluble in hydrochloric acid. Nitric acid oxidizes it to antimony trioxide or *antimonic acid*, H_3SbO_4 .



With *aqua regia* antimony reacts, giving *antimony trichloride*. When the solution is distilled it gives the trichloride as a liquid boiling at 223° C. This solidifies to a pasty mass called "butter of antimony."

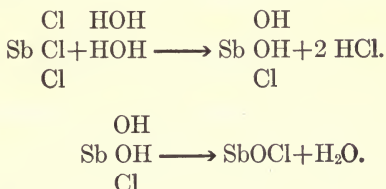
Concentrated sulphuric acid reacts with antimony. The products are shown in the equation,



Antimony resembles arsenic and phosphorus on the one hand and bismuth on the other. It is like the former elements in the general structure of its compounds; like the latter in its ability to form a salt with sulphuric acid and in other *metallic* properties.

Its positive (+) properties are, however, *weak*, as is indicated by the easy decomposition of its salts by water.

Thus, antimony trichloride is decomposed by much water, giving a *basic* chloride (its simplest formula is SbOCl) and hydrochloric acid.



Again, although antimony trioxide reacts with *concentrated* sulphuric acid, giving antimony sulphate, $\text{Sb}_2(\text{SO}_4)_3$, yet when antimony trioxide reacts with the *dilute* acid, the product has the formula $(\text{SbO})_2\text{SO}_4$. The compound SbOCl may be called *antimony oxy-chloride* or *antimonyl chloride*, the group SbO being called *antimonyl*. The compound having the formula $(\text{SbO})_2\text{SO}_4$ is, therefore, *antimonyl sulphate*.

Antimony, even more than arsenic, is a *transition* element. Its oxide, Sb_2O_3 , reacts not only with acids, giving antimony salts, but also with *alkalies*, giving salts of *antimony acids*. Thus, antimony trioxide gives with sodium hydroxide *sodium antimonite*, Na_3SbO_3 . This is a salt of *antimonious acid*, which corresponds with phosphorous and arsenious acids.

369. Other Antimony Compounds. — Among the important antimony compounds are *hydrogen antimonide* (or *stibine*), *tartar emetic*, and *antimony trisulphide*.

Hydrogen antimonide, SbH_3 , is formed from an antimony compound just as *hydrogen arsenide* is formed from an arsenic compound, namely, by reduction with *nascent* hydrogen (cf. § 361).

Marsh's test may be carried out with antimony in the apparatus used for arsenic (Fig. 80). When, however, hydrogen sulphide is passed over the antimony mirror, the antimony sulphide formed is *black*, while that of arsenic is *yellow*. Again, when hydrochloric acid gas is passed through the tube, the antimony sulphide forms drops of *antimony trichloride*, while the arsenic trisulphide is unchanged. We can thus distinguish between arsenic and antimony.

Tartar emetic is *potassium antimonyl tartrate*, $\text{K.SbO.C}_4\text{H}_4\text{O}_6$. It is formed by heating a mixture of antimony trioxide, potassium hydrogen tartrate (cream of tartar), and water. It is used in medicine.

Antimony trisulphide, Sb_2S_3 , is formed by treating solutions of either antimonious salts or antimonites with hydrogen sulphide. Two isomeric antimony trisulphides are known. The one formed by precipitation is brick-red, while *stibnite* is black. The red form is unstable; it goes over into the black form *with evolution of heat*.

The precipitate of antimony trisulphide reacts readily with alkaline sulphides giving *sulphantimonites*, just as arsenic trisulphide gives *sulpharsenites* (cf. § 365). The sulphantimonites are decomposed by dilute acids; and antimony trisulphide is reprecipitated.

370. Uses of Antimony. — Antimony is used in making alloys. Examples are: Printer's type-metal, pewter, and Britannia metal. *Antimony black* is a finely divided form of the metal; plaster casts are rubbed with it to give them a metallic coating.

D. Bismuth.

371. Preparation of Bismuth. — Bismuth is found in nature *free* and also in the form of the sulphide (Bi_2S_3) and the oxide (Bi_2O_3). It is prepared from its sulphide as antimony is, namely, by first *roasting* the sulphide to form the oxide, and then *reducing* the oxide.

To get bismuth free from impurities, such as arsenic, etc., it is mixed with saltpeter and heated. The impurities are thus oxidized to compounds soluble in water, and can be separated from the bismuth.

372. Properties. — In its physical appearance bismuth is much like antimony, but it has a slightly *reddish* color. Its melting temperature is $265^{\circ}\text{C}.$, and its specific gravity about 10. It boils at $1700^{\circ}\text{C}.$

Bismuth burns in the air when at red heat; the product is the trioxide, Bi_2O_3 .

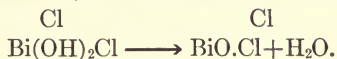
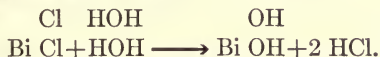
Bismuth trioxide is formed, also, by heating the nitrate $\text{Bi}(\text{NO}_3)_3$ (see § 230), and by heating the hydroxides $\text{Bi}(\text{OH})_3$ and BiO.OH , which are produced when potassium hydroxide solution is added to a solution of a bismuth salt.

Unlike the trioxides of arsenic and antimony, bismuth trioxide has *not* the ability to react with alkalies to form salts. It is an entirely *basic* oxide. The higher oxide of bismuth, Bi_2O_5 , has slightly acidic properties; for it is the anhydride of *bismuthic acid*, HBiO_3 . The acid is, however, very weak and very unstable.

Bismuth forms no hydrogen compound corresponding to ammonia, phosphine, arsine, and stibine.

373. Bismuth Salts. — Bismuth combines with the halogens, giving tri-halogen compounds, which correspond to those of arsenic and antimony. It reacts with nitric acid to give the *nitrate*, $\text{Bi}(\text{NO}_3)_3$; with *aqua regia* to give the *chloride*, BiCl_3 , and with concentrated sulphuric acid to give the sulphate, $\text{Bi}_2(\text{SO}_4)_3$.

Bismuth salts, like those of antimony, are decomposed by much water, giving the *basic salt* and free acid. The trichloride usually decomposes as follows: —



The nitrate decomposes in a similar way.

When *hydrogen sulphide* is added to the solution of a bismuth salt there is produced an almost black precipitate of *bismuth sulphide*, Bi_2S_3 . This is insoluble in alkaline sulphides.

374. Uses of Bismuth. — The principal use of bismuth is as an ingredient of alloys. Its chief alloys are *Wood's metal* and *Rose's metal*.

Wood's metal consists of *four* parts, by weight, of bismuth, *one* each of tin and cadmium, and *two* of lead. It melts at about 65°C. ; hence it is much used for metal baths in the laboratory.

Rose's metal contains nine parts of bismuth to one each of lead and tin; it melts at 94°C.

The *basic nitrate* of bismuth (simplest formula, BiO.NO_3) is used in medicine under the name *bismuth sub-nitrate*.

375. The Nitrogen Family. — The elements nitrogen, phosphorus, arsenic, antimony, and bismuth, together with some *rare* elements, form a natural family, just as the halogens do; for in this, the nitrogen family, just as in the case of the halogens,

we have a series of elements exhibiting a gradation of properties in the order of the atomic weights. The table on the next page shows this for some properties.

A complete list of the properties of the members of the nitrogen family will not agree so well as in the case of the halogens. When, however, we can compare corresponding compounds having the same number of atoms to the molecule, a fair degree of regularity exists.

376. Exercises.

1. What means are there of kindling fires without the use of phosphorus?

2. How much phosphorus is there in 440 grams (about one pound) of bone-ash, if 70% of the ash is $\text{Ca}_3(\text{PO}_4)_2$?

3. Express the hydrolysis of antimony and bismuth chlorides by equilibrium equations. Would hydrolysis be favored by the presence of much or little acid? Much or little water? How get the basic chlorides into solution?

4. Write the formulas of the following substances: *normal barium phosphate*, *primary ammonium phosphate*, *potassium hypophosphite*, *strontium metaphosphate*, and *silver pyrophosphate*.

5. Why is it undesirable that arsenic compounds should be used to color wall papers? Explain.

6. Show by an equation the reduction of arsenic trioxide by nascent hydrogen to *arsine*. The combustion of *arsine*.

7. When a bath of Wood's metal is being melted the unmelted metal floats upon the liquid portion. Compare the specific gravity of the solid with that of the liquid. Will the liquid expand or contract on solidifying?

ELEMENT.	Nitrogen.	Phosphorus.	Arsenic.	Antimony.	Bismuth.
ATOMIC WEIGHT.	14	31	75	120	207
SPECIFIC GRAVITY.	0.885 (liquid).	1.83 to 2.19	4.7 to 5.7	6.7	9.9
BOILING TEMPERATURE.	-194° C.	287°	450°	1500°	1300°
BOILING TEMPERATURE OF TRICHLORIDE.	Not known, but low.	76°	130°	223°	447°
PROPERTIES OF TRIOXIDES.	N ₂ O ₃ is anhydride of nitrous acid.	P ₂ O ₃ is anhydride of phosphorous acid. Weaker than nitrous acid.	As ₂ O ₃ is both weakly acid and weakly basic.	Sb ₂ O ₃ is like As ₂ O ₃ .	Bi ₂ O ₃ has only <i>basic</i> properties.
PROPERTIES OF PENTOXIDES.	N ₂ O ₅ is anhydride of nitric acid.	P ₂ O ₅ is anhydride of phosphoric acid. Weaker than nitric acid.	As ₂ O ₅ is anhydride of arsenic acid. Weaker than phosphoric acid.	Sb ₂ O ₅ is anhydride of antimoniac acid.	Bi ₂ O ₅ has only <i>faintly</i> acid properties.
HYDROGEN COMPOUNDS.	NH ₃ unites with HCl, HI, etc., to form salts.	PH ₃ unites with acids with difficulty.	AsH ₃ does not unite with acids.	SbH ₃ does not unite with acids.	BiH ₃ is not known to exist.

CHAPTER XXVII.

THE PERIODIC SYSTEM.

377. Natural Families. — During the first half of the nineteenth century various attempts were made to classify the elements. Chemists recognized the fact that there were “natural families” of elements, and that the members of the same family (called **homologous** elements), while bearing a *general* resemblance to one another, yet showed a regular *gradation* of properties in the order of the atomic weights.

We have already described two of these families, viz., the *halogen* family (*cf.* § 335) and the *nitrogen* family (*cf.* § 375).

Other natural families exist. Thus, sulphur and oxygen, with the rarer elements *selenium* (Se) and *tellurium* (Te) form a group of homologous elements. The atomic weights are, —

O, 16; S, 32; Se, 79; Te, 127.

Again, the elements *lithium*, *sodium*, and *potassium*, with the rare elements *rubidium* and *cæsium*, form the well-known “**alkali**” group of metals. The atomic weights of the three more common metals of the family are, —

Li, 7; Na, 23; K, 39.

Here, as in the case of the halogens, we find a continuous gradation of properties in the order of the atomic weights.

Lithium hydroxide, LiOH , is a weaker base than sodium hydroxide, NaOH ; while potassium hydroxide, KOH , is the strongest base of the three.

378. The Periodic Arrangement. — Although the connection between the properties and the atomic weights of elements in the *same group* had been recognized for years, it was left to the Russian chemist *Mendelejeff* and the German chemist *Lothar Meyer* to discover, in 1869 to 1871, a new and peculiar relation between the properties of *all* elements and their atomic weights. This relation is the basis of the **Periodic System**.

Let us write the symbols of the first *sixteen* elements *in the order of the atomic weights*. Omitting *hydrogen*, which for the present stands almost unrelated, we have, —

<i>Element,</i>	Li	Gl(Be)	B	C	N	O	F	Na	Mg	Al
<i>Atomic Wt.,</i>	7	9	11	12	14	16	19	23	24	27
<i>Element,</i>	Si	P	S	Cl	K	Ca.				
<i>Atomic Wt.,</i>	28	31	32	35.5	39	40				

A study of the elements from *lithium* to *fluorine*, inclusive, shows that there is a regular gradation of properties. The strongly **metallic** properties of *lithium* are weaker in *glucinum*, and yet weaker in *boron*. The *hydroxide* of boron is, in fact, called *boric acid*. In *carbon* we have an element with faintly *electro-negative*, i. e., non-metallic, properties; the elements *nitrogen* and *oxygen* are still more *electro-negative*; until in *fluorine* we have a **typical**

non-metal, and probably the most electro-negative substance known.

The increase of atomic weight from 7 to 19 has thus continuously *diminished* the electro-positive, or metallic, character possessed by lithium, and has *increased* the electro-negative character typified by fluorine.

But after fluorine the gradation of properties does not continue; for the element *sodium*, the next greater in atomic weight, is, like lithium, one of the most typical *metals*. There is, in fact, a sudden "reversion to type"; for sodium belongs in the same natural family with lithium.

Let us, then, *proceed* in the order of atomic weight, writing the *second* set of seven elements under the first set, as in the table in § 379. *Sodium* will be under *lithium*, *magnesium* under *glucinum*, etc. We find the same gradation of properties with increase of atomic weight from *sodium* to *chlorine* as we found from *lithium* to *fluorine*.

Magnesium, like sodium, is a metal; but magnesium hydroxide is a weaker base than sodium hydroxide. *Aluminum*, the next in the order of atomic weight, is also metallic; but its hydroxide is either a base or an acid, according to circumstances. In *silicon*, the next element, metallic properties are *wanting*; silicon forms *silicic acid*. Next come *phosphorus* and *sulphur*, undoubted non-metals; and then *chlorine*, the first homologue of fluorine.

The element following chlorine is *potassium*; its atomic weight is 39. Potassium is a *typical*

metal, and belongs in the same family with lithium and sodium. In passing from chlorine to potassium we have, therefore, a second instance of “reversion to type.”

The properties of calcium are less metallic in character than those of potassium; for calcium hydroxide is a weaker base than potassium hydroxide. Thus, after potassium, as after sodium, variation in the properties of the elements goes on *continuously with increase of atomic weight* for another period.

From the study of “natural families” we learned that the properties of the elements in any one family vary *continuously* with the atomic weight; now we see that the properties of **all** elements, while not varying *continuously*, as in the natural family, yet vary *periodically* with the atomic weight. That is to say, a certain *increase* of atomic weight is accompanied by a *recurrence* of certain properties possessed by an element of *lower* atomic weight. The facts are summed up in what is often called the **Periodic Law**, which is, “*The properties of the elements are periodic functions of their atomic weights.*”

379. Regularities in the Periodic Arrangement. —

If we write down the symbols of the elements from lithium to calcium, putting *similar* elements in the same *vertical* columns, we have an arrangement like the following: —

Li (7)	Gl or Be (9)	B (11)	C (12)	N (14)	O (16)	Fl (19)
Na (23)	Mg (24)	Al (27)	Si (28)	P (31)	S (32)	Cl (35.5)
K (39)	Ca (40)					

In this table we observe several regularities:—

(1) After every period of *seven* elements a second period of *seven* begins.

(2) The difference between the first and the eighth, the second and the ninth, etc., elements is in every case nearly *sixteen* units. Two successive elements of the same family are thus separated by *six* intervening elements, and differ from each other by about sixteen units of atomic weight.

(3) Elements in adjacent positions in the horizontal rows, i. e., *heterologous* elements, differ from one another by *small* numbers of units, generally only *one* or *two*. The *largest* differences occur between fluorine and sodium and between chlorine and potassium, i. e., at the *break* in the periods.

380. Properties of an Element Determined.—

We may call the two elements adjacent to another element in the horizontal rows the *adjacent heterologues* of the element. Thus, *boron* and *nitrogen* are the adjacent heterologues of *carbon*. The two adjacent heterologues and the two adjacent *homologues* of an element may be called the *analogues* of the element. Thus, *glucinum*, *sodium*, *calcium*, and *aluminum* are the analogues of *magnesium*.

Mendelejeff showed that if the properties of magnesium were wholly unknown they could be deduced approximately from the properties of its four *analogues*.

Thus, the *atomic weight* of magnesium (24) is very nearly the *average* of the atomic weights of its analogues.

$$\frac{9+40+23+27}{4} = 24.75.$$

Again, the average of the *specific gravities* of the analogues of magnesium gives approximately the specific gravity of magnesium itself. The specific gravities of sodium, aluminum, glucinum, and calcium are 0.97, 2.56, 2.10, and 1.58, respectively. The average is 1.8. Experiment shows the specific gravity of magnesium to be 1.75.

Up to the time of Mendelejeff and Meyer, the existence of an element with any particular properties was regarded as an *isolated* and *accidental* fact in nature; but the periodic arrangement presents the idea that it is necessary that elements of given atomic weight shall have certain definite properties.

381. "Gaps" in the Periodic Arrangement. — When Mendelejeff first drew up his table of the elements, he found that in several cases neighboring heterologous elements did not fall *into place*, i. e., into the vertical rows containing the other members of their natural families. Thus, the element *zinc* (65) was followed by *arsenic* (75). The interval is large, viz., *ten* units. Now, zinc belongs in the same natural family with *magnesium*; and if arsenic follows zinc, arsenic must belong to the family of *boron* and *aluminum*. Hence the *second* and *fourth* horizontal rows would be as follows: —

2. Na (23) Mg (24) Al (27) Si (28) P (31) S (32) Cl (35.5)
4. Cu (63) Zn (65) As (75) Se (79) Br (80), etc.

This arrangement is manifestly *impossible*; for by all its properties *bromine* belongs with *chlorine*, *selenium* with *sulphur*, and *arsenic* with *phosphorus*.

The arrangement of the second and fourth rows *should* be, —

2. Na (23) Mg (24) Al (27) Si (28) P (31) S (32) Cl (35.5)
 4. Cu (63) Zn (65) — — — As (75) Se (79) Br (80)

There were, therefore, two *gaps* in the *fourth* row; a member of the *aluminum* family and a member of the *silicon* family were wanting.

382. Prediction of Unknown Elements. — Reasoning from the assumption that the properties of an element are determined by its position in the periodic grouping, Mendelejeff drew up a table stating the properties of the unknown elements that ought to exist to fill the gaps in the fourth row. The supposed element of the *aluminum* family he called **ek-aluminum**, and that of the *silicon* family, **eka-silicon**. Another gap existed in the *third* row, between *calcium* (40) and *titanium* (48). To this element Mendelejeff gave the provisional name **eka-boron**.

Mendelejeff and Meyer's tables were published in 1871. Four years afterward an element having the properties of *ek-aluminum* was discovered in France, and named **Gallium**. Its atomic weight was found to be 70, as predicted.

In 1880, Nilson and Cleve discovered in a Scandinavian mineral a new element which had the properties of *eka-boron*. They called it **Scandium**.

In 1886, Clemens Winkler discovered the element which he called **Germanium**. Upon comparing the properties of this element (atomic weight 72) with those foretold for *eka-silicon*, he decided that the

new element could be nothing else than the eka-silicon predicted by Mendelejeff fifteen years before.

Other elements, more recently discovered, have also been found places in the periodic table. Thus *radium* (at. wt. 226.4) fills the space below mercury.

383. The Periodic Table.

The periodic table is given on the following page. If we include the **Zero** group, we have **nine** groups. The group marked VIII consists of three sub-groups of three elements each. These do not fit into the table elsewhere. Each sub-group consists of closely related elements. In *osmic acid anhydride*, OsO_4 , we have an element with a **valence of 8**.

The elements of Group IV reach the *highest valence toward* hydrogen, i. e., 4. From Group IV to Group VII the valence toward hydrogen *decreases*. The valence of the elements toward oxygen *increases* from Group I to Group VIII.

R is a *general symbol* for all the elements.

384. The Argon Family.

The discovery of the Argon family (*cf.* § 192) introduced a new group, the **Zero Group**, into the periodic table. Helium comes before lithium; neon before sodium, etc. The elements of this group are all monatomic (*cf.* § 142), and their valence is, apparently, **zero**.

385. Conclusion.— Besides resulting in the *prediction* of the properties of undiscovered elements, the periodic classification has led to a more careful study of the atomic weights of *known* elements.

The classification has many *faults*, but it is full of suggestions, and shows a *striking* relationship between

The Periodic Arrangement. (Revised to 1912.)

SERIES.	ZERO GROUP.	GROUP I. — R ₂ O	GROUP II. — RO	GROUP III. — R ₂ O ₃	GROUP IV. RH ₄ RO ₂	GROUP V. RH ₃ R ₂ O ₃	GROUP VI. RH ₂ RO ₃	GROUP VII. RH R ₂ O ₇	GROUP VIII. — RO ₄
1		H = 1.008							
2	He = 3.99	Li = 6.94	Cl = 9.1	B = 11.0	C = 12.00	N = 14.01	O = 16.00	F = 19.0	
3	Ne = 20.2	Na = 23.00	Mg = 24.32	Al = 27.1	Si = 28.3	P = 31.04	S = 32.07	Cl = 35.46	
4	A = 39.88	K = 39.10	Ca = 40.07	Sc = 44.1	Ti = 48.1	V = 51.0	Cr = 52.0	Mn = 54.93	Fe = 55.84. Co = 58.97. Ni = 58.68.
5		Cu = 63.57	Zn = 65.37	Ga = 69.9	Ge = 72.5	As = 74.96	Se = 79.2	Br = 79.92	
6	Kr = 82.92	Rb = 85.45	Sr = 87.63	Y = 89.0	Zr = 90.6	Cb = 93.5	Mo = 96.0		Ru = 101.7. Rh = 102.9. Pd = 106.7.
7		Ag = 107.88	Cd = 112.40	In = 114.8	Sn = 119.0	Sb = 120.2	Te = 127.5	I = 126.92	
8	Xe = 130.2	Cs = 132.81	Ba = 137.37	La = 139.0	Ce = 140.25	Pr = 140.6	Nd = 144.3		
9		Sa = 150.4		Gd = 157.3	Tb = 159.2		Er = 167.7		
10		Tm = 168.5		Yb = 172.0		Ta = 181.5	W = 184.0		Os = 190.9. Ir = 193.1. Pt = 195.2.
11		Au = 197.2	Hg = 200.6	Tl = 204.0	Pb = 207.10	Bi = 208.0			
12			Ra = 226.4		Th = 232.4		U = 238.5		

the elements. Because of this relationship chemists are tending to the belief that all the elements are modifications of some yet simpler forms or form of matter. As to the character of this fundamental substance, nothing is known at present. A recent irregularity in the periodic arrangement results from the fact that the atomic weight of tellurium has been placed at 127.5, or slightly higher than iodine, 126.9, and that argon (39.88) comes before potassium (39.10). This is not startling, however, for the periodic recurrence of properties is only *approximate*, at the best.

386. Exercises.

1. The *specific gravities* of some elements are as follows: P (red), 2.14; Cl (liquid), 1.33; Cd, 8.6; In, 7.4; Te, 6.2. Using these figures and those in Appendix v, see if there is a relation between specific gravity and atomic weight in Series 3 (begin with Na), and in Series 7.

2. Three elements that appear upon the list of International Atomic Weights, but are not in the periodic table, are *dysprosium* (Dy=162.5), *europium* (Eu=152), and *lutecium* (Lu=174). Are there places for them? Is the existence of a blank in the proper place the only condition necessary for placing elements in particular groups?

3. If dysprosium belongs where its atomic weight places it, what is the formula of its oxide, chloride, and nitrate? If europium belongs in a blank, according to its atomic weight, what will be the formulas of its hydroxide, carbonate, sulphide, sulphate, and nitrate? Answer the same questions for lutecium.

4. What two kinds of elements might fill the blank in Series 6, Group VII? What atomic weight belongs in this space?

CHAPTER XXVIII.

SILICON AND BORON.

A. Silicon.

387. Occurrence of Silicon. — As was stated in § 9, silicon is, next to oxygen, the most abundant constituent of the earth's crust. It is not found free, but in the form of its oxide, SiO_2 , and in *silicates*, i. e., the salts of *silicic acid*. Silicon dioxide (silica) and the silicates make up sand, clay, and almost all the crystalline rocks of the earth's crust.

Silica is taken up by plants. The *straw* and *husks* of the grains contain it. The *equisetum* is called "scouring-rush," from the large amount of silica present in it. Silica is found, also, in the skin, nails, hair, etc., of animals.

Certain microscopic plants, the **diatoms**, have skeletons of silica; and these have accumulated in large deposits in some places.

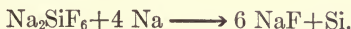
388. Preparation. — Silicon, like carbon, exists in several *allotropic* forms. The **amorphous** variety may be obtained by heating a mixture of powdered *quartz* and powdered *magnesium*.



Amorphous silicon is a brown powder which burns, when heated in the air, to silicon dioxide. It is attacked by *hydrofluoric acid*, but not by other acids.

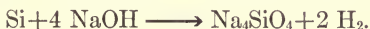


Silicon is obtained **crystalline** by heating *sodium fluosilicate*, Na_2SiF_6 , with sodium and zinc.

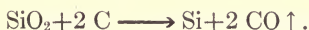


The silicon dissolves in the melted zinc, and separates out in crystals as the zinc cools. When the zinc solidifies it encloses the silicon. The zinc is then removed by treating the mass with hydrochloric acid; and silicon remains.

The crystalline form of silicon does not burn in air or oxygen, nor does it dissolve in acids. It dissolves in hot sodium hydroxide solution, giving *sodium silicate* and hydrogen. The simplest equation is, —

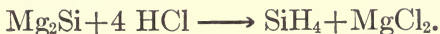


Silicon is made on a large scale, at Niagara, by heating quartz sand with coke in the electric furnace. It is used in making steel (*cf.* § 488).

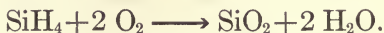


389. Silicon Compounds. — The general structure of silicon compounds is like that of the corresponding carbon compounds. *Hydrogen silicide*, SiH_4 , corresponds to *marsh gas*, CH_4 ; *silicon tetrachloride*, SiCl_4 , to *carbon tetrachloride*, CCl_4 ; *silicon dioxide*, SiO_2 , to *carbon dioxide*, CO_2 ; *silicic chloroform*, SiHCl_3 , to *chloroform*, CHCl_3 .

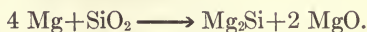
Hydrogen silicide is a colorless gas. It may be obtained, mixed with hydrogen, by treating *magnesium silicide* with dilute hydrochloric acid.



As ordinarily made, it ignites *spontaneously* in the air.

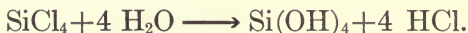


Magnesium silicide is prepared by heating powdered quartz with an *excess* of magnesium powder.



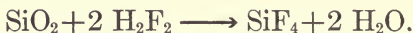
If too little magnesium is used, amorphous silicon results (*cf.* § 388).

Silicon tetrachloride is a colorless liquid, boiling at 59° C. It is formed from silicon and chlorine. Water decomposes it, giving *silicic acid* and *hydrochloric acid*.

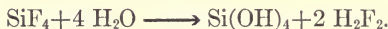


(*Cf.* the action of *phosphorus trichloride* with water, § 354.)

Silicon tetrafluoride is a colorless gas, formed when silicon dioxide is treated with hydrofluoric acid.



Silicon tetrafluoride is decomposed by water as the *tetrachloride* is.

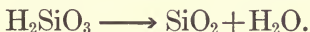


Instead of being set free, however, the hydrofluoric acid unites with some of the silicon tetrafluoride, forming **fluosilicic acid**, H_2SiF_6 . The name "fluosilicic acid" means *silicic acid*, H_2SiO_3 , with its *oxygen* replaced by fluorine, — *three* bivalent oxygen atoms by *six* univalent fluorine atoms (*cf.* § 365, *sulpharsenites*, and § 268, *thiosulphates*). Many *fluosilicates* are known; potassium fluosilicate, K_2SiF_6 , is one of the few difficultly soluble potassium salts.

390. Silicon Carbide. — Silicon carbide (SiC) or **carborundum** is among the three hardest substances known, the others being *boron carbide* and the diamond. It is made by heating a mixture of powdered quartz, coke, saw-dust, and common salt in the electric furnace.

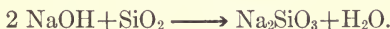
Carborundum is not attacked by acids nor by solutions of alkalis. It burns only with great difficulty. Because of its hardness, powdered carborundum is used as a polishing and cutting agent.

391. Silicon Dioxide. — Silicon dioxide is found as sand, quartz, etc. (*cf.* § 387). The pure substance may be prepared by heating silicic acids, H_4SiO_4 , H_2SiO_3 , etc.



Silicon dioxide is thus *silicic anhydride*.

When any form of silicon dioxide is fused with sodium or potassium hydroxide or carbonate, sodium or potassium *silicate* results.



Calcium carbonate acts in the same way.

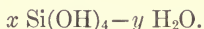
When silica is fused with the *oxide* of a metal, a silicate is also formed (*cf.* § 162).



Acids do not act upon silica (except hydrofluoric acid as in § 389).

392. Silicic Acid. — When a soluble silicate is treated with hydrochloric acid, a bulky mass, like gelatine, is precipitated. This probably consists of *orthosilicic* acid, H_4SiO_4 . When the gelatinous mass is dried at the ordinary temperature, it loses water and becomes a non-crystalline powder. This is probably *ordinary* silicic acid, H_2SiO_3 . When the powder is heated to a *high* temperature it loses water, forming silica, SiO_2 . The equations are given in § 391.

Polysilicic Acids. — Besides the ortho and ordinary forms of silicic acid, many other forms are possible; these are known as **polysilicic** acids. They are derived from orthosilicic acid by the loss of different proportions of water. A general formula for them all would be, —



Thus, if $x=2$ and $y=1$, we have, —



Among the varieties of *amorphous* silica found in nature are *agate*, *chalcedony*, *opal*, *carnelian*, *flint*, *amethyst*, etc. These all contain *water*, and may, therefore, be looked upon as forms of the polysilicic acids. The colors of these substances are usually due to traces of impurities.

393. Silicates. — The silicates are salts of silicic acid. The mineral *chrysolite* is *magnesium silicate*, Mg_2SiO_4 . *Serpentine* is $\text{Mg}_3\text{Si}_2\text{O}_7$. These are salts of the acids H_4SiO_4 and $\text{H}_6\text{Si}_2\text{O}_7$, respectively. *Potassium*, *sodium*, and *calcium silicates* are derived from the acid H_2SiO_3 .

Potassium and sodium silicates are known as "water glass"; they are used to make cements and artificial stone. **Kaolin** is practically pure aluminum silicate, $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$. It fuses at a very *high* temperature. It is used for making china and crockery ware, fire-bricks, etc. **Clay**, which is *impure* aluminum silicate, melts lower than kaolin; it is used for making pottery, bricks, etc. The red color of baked clay is due to *ferric silicate*, $\text{Fe}_2(\text{SiO}_3)_3$.

394. Glass. — Glass is a mixture of certain *silicates*, generally of sodium or potassium silicate with calcium or lead silicate. Silicon dioxide is also present.

The silicates of calcium, lead, etc., *crystallize* when they solidify; a glass made from them would break into fragments on cooling. The silicates of sodium and potassium, however, not only do not crystallize themselves, but even *prevent the other silicates from crystallizing*.

Ordinary, soft glass, such as is used for window panes and bottles, is essentially a mixture of the silicates of *calcium* and *sodium*. It is made by melting together *silica*, *calcium carbonate*, and *sodium carbonate*, in fire-clay pots about 4 feet high and 4 feet in diameter. Carbon dioxide escapes.

Hard glass is a mixture of the silicates of *calcium* and *potassium*. It is used for making chemical apparatus, lamp globes, etc. **Crown glass** is a variety of it. **Jena glass** is a hard glass containing boron trioxide.

Flint glass, such as is used in making optical instruments, etc., is a mixture of *potassium and lead silicates*.

Enameled or "**milky**" glass is made by adding *cryolite* (cf. § 316), tin oxide, etc., to ordinary glass.

"**Granite ironware**" or "*porcelain-lined*" ware consists of iron covered with an easily fusible glass, called *enamel*.

Color is imparted to glass by the addition of small amounts of other substances. Thus, a *cobalt* compound colors glass blue; a *cuprous* compound, *red*; a *chromic* compound, *green*.

The **etching** of designs on glass is done with *hydrofluoric acid*, as described in § 318, or with a sand blast.

Window glass is made by blowing the viscous material from the melting pots into hollow cylinders several feet long, and about $1\frac{1}{2}$ feet in diameter. These are cut open lengthwise, and flattened out in ovens.

Plate glass is made by pouring melted glass upon iron plates, and rolling it out with heated rollers. The plates are then ground and polished.

Bottles, etc., are made by attaching lumps of the viscous glass to hollow tubes, and blowing the glass out in molds.

Pressed glassware is made in molds; in **cut** glassware the designs are ground or polished by means of *emery*, *carborundum*, or *sandstone* wheels. All articles of glass, to be permanent, must be **annealed**. Annealing consists in allowing the hot object to cool *regularly*, so that its molecules may assume *permanent* positions with reference to one another. Unannealed glass may fly to pieces at the slightest jar.

B. Boron.

395. Occurrence of Boron. — The element *boron* is the first member of the aluminum group of elements (*cf.* § 383); yet in its free state it closely resembles silicon and carbon. It occurs in nature chiefly as *boric acid* (H_3BO_3) and as *borax* ($\text{Na}_2\text{B}_4\text{O}_7$).

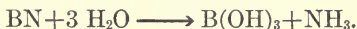
Boric acid is found chiefly in Tuscany, where it issues, mixed with steam, from the earth. Borax is found in Nevada and California in dry borax lakes. *Boracite*, $(\text{Mg}_3\text{B}_3\text{O}_{15})_2 \cdot \text{MgCl}_2$, occurs at Stassfurt, in Germany.

396. Preparation. — Boron exists in *two* allotropic forms, — the *amorphous* and the *crystalline*; it is difficult to prepare either form in a pure state.

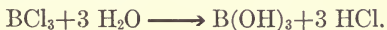
Crystalline boron is made by heating boron trioxide, B_2O_3 , with aluminum. The aluminum reduces the oxide; and the liberated boron dissolves in the excess of aluminum. When the cooled mass is treated with hydrochloric acid, the aluminum dissolves, leaving crystals of boron.

397. Properties. — Crystalline boron has a specific gravity of 2.6, and resembles the diamond. The *amorphous* form is brown. It *burns* when heated in the air, giving *boron trioxide*, B_2O_3 . Nitric acid converts it into boric acid. The crystalline form is more difficult to ignite than the amorphous.

Boron dissolves in melted sodium hydroxide, giving sodium borate. When it is heated in nitrogen or ammonia it gives *boron nitride*, BN. This is a white powder which is decomposed by steam, giving *boric acid* and *ammonia*.



With chlorine, boron forms *boron trichloride*, BCl_3 , a colorless liquid. This is decomposed by water, giving boric acid and hydrochloric acid (*cf.* §§ 354 and 389).

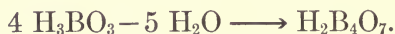


398. Boric Acid. — Boric acid is made by adding concentrated hydrochloric or nitric acid to a hot solution of borax. It is a white, crystalline solid. Its aqueous solution has a faintly acid reaction with litmus, but colors *turmeric* paper *brown*, just as

sodium hydroxide does. Boric acid is in some respects like *aluminum hydroxide*, which is an acid or a base, according to circumstances.

Boric acid is *volatile with steam*, as was indicated in § 395. Its solution in ethyl alcohol burns with a bright green flame. When boric acid is heated it loses water, giving finally the *anhydride*, B_2O_3 . This redissolves readily in water, giving the acid.

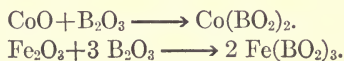
399. Borax. — The ordinary *borates* are derived not from the *ortho* acid, H_3BO_3 , but from *tetraboric* acid, $H_2B_4O_7$. This is related to the *ortho* acid just as the *polysilicic acids* are to *orthosilicic acid* (*cf.* § 392).



Borax is **sodium tetraborate**, $Na_2B_4O_7$. It comes into the market as crystals which are either $Na_2B_4O_7 \cdot 10 H_2O$ or $Na_2B_4O_7 \cdot 5 H_2O$.

When heated, borax loses its crystal-water and swells to a porous mass; on stronger heating, this melts to a clear glass. Molten borax dissolves the oxides of metals, and with some of them gives characteristic colors; hence, its use in the *laboratory* to form the "borax bead," and in the *arts* to clean the surfaces of metals before *soldering* and *welding*, and before coating metals with enamel (*cf.* § 394).

We may look upon the borax molecule as $2 NaBO_2 + B_2O_3$, *i. e.*, as sodium *metaborate* plus *boron trioxide*. The oxides of metals react with the boron trioxide to give other metaborates (*cf.* §§ 162, 357, and 391).



Borax is used, also, to prevent the decomposition of organic substances, in medicine, in the manufacture of hard-water soaps, and to increase the gloss of starch.

400. Exercises.

1. Name some of the scouring mixtures which consist essentially of silica.

2. Suggest a *possible* reason for the fact that silicon dioxide is a hard, infusible solid, while the corresponding oxide of carbon is gaseous.

3. Name some polishing, or *abrasive*, agents besides silica and carborundum. How are diamonds polished?

4. From some of the facts named in this chapter suggest a way in which carbon dioxide might be liberated from calcium carbonate in the earth's crust.

5. What class of substances must be present in underground waters so that *silica* may be held in solution? What substance is needed to hold *calcium carbonate* in solution?

6. From what polysilicic acid would a silicate of the formula CaSi_2O_5 be derived? Show the relation of this acid to normal silicic acid.

7. What are the proportions, *by volume*, of factors and products in the equation representing the combustion of *hydrogen silicide* (*cf.* § 389)?

CHAPTER XXIX.

METALS.

401. Metals and Non-Metals. — In our previous work we have studied chiefly *non-metallic* elements. There is, however, no sharp distinction between metals and non-metals, but rather a gradual change from one class to the other (*cf.* § 378). But just as *oxygen*, *chlorine*, and *sulphur* have a *distinct* character, which no one would mistake for that of a metal, so there are certain elements having a *typical* metallic nature.

Metals are usually opaque, and their polished surfaces are good reflectors of light; hence the **metallic luster**. They are good conductors of heat and electricity. With oxygen and hydrogen the metals form *bases*, and by replacing the hydrogen of acids, i. e., *ionic* hydrogen, they form *salts*.

Some elements, e. g., antimony, are both acid-forming and base-forming; they are often called **metalloids**.

Besides the *general* properties already given, metals possess other properties in varying degrees. Thus, some metals, e. g., *sodium* and *lead*, are soft; while others, e. g., *chromium* and *manganese*, are hard. *Sodium* and *lithium* are light enough to float on water; while gold is 19.3, and platinum 21.5 times as heavy as water. Metals having a specific gravity less than 5 are called "light" metals; those above 5 are called "heavy" metals.

402. Occurrence and Extraction of Metals.—

The solid elements and compounds found in nature are called **minerals**. The minerals and mixtures of minerals from which metals are obtained are called **ores**. Some metals, e. g., *gold* and *copper*, occur *free*, that is, *uncombined* with other elements; but most metals are found as *oxides* or *sulphides*. Some occur as *carbonates*, *hydroxides*, *chlorides*, *sulphates*, *phosphates*, etc.

If metals occur **free**, they may be separated by mechanical means from minerals mixed with them. An illustration is the crushing of an ore in a stamp-mill, and the washing away of the lighter materials. *Copper* and *gold* are extracted in this way, although *chemical* methods are employed with inferior ores of these metals.

The most **common** method of extracting metals is to reduce the **oxide** with carbon (charcoal or coke). This is the case with iron. If the ores used are not oxides, they are usually converted into oxides by "roasting" (*cf.* § 252). *Sulphides*, *hydroxides*, and *carbonates* may thus be changed into *oxides*.

Another method of reducing an oxide is to heat it in a stream of *hydrogen*. The oxygen and hydrogen unite and escape as *steam*, while the metal is left. This is a good *laboratory* method; but it is too expensive for commercial use.

Chlorides are sometimes reduced by heating them with *sodium*. *Aluminum* was *formerly* obtained in this way from its chloride.

Several of the metals, e. g., *aluminum*, *sodium*, and *calcium*, are obtained by the action of the **electric current** upon some of their compounds.

403. Alloys. — When two or more melted metals form a uniform mixture (*cf.* § 78), the mixture is called an **alloy**. If *mercury* is one of the metals, the alloy is called an **amalgam**. Alloys resemble solutions in many ways. Thus, melted tin and lead, like alcohol and water, mix in any proportion, but zinc and lead, like ether and water, only to a limited extent (*cf.* § 82). If a metal is mixed with even a small per cent of another, it undergoes a marked change in properties; the melting temperature, the malleability, and the conductivity for heat and electricity are lowered (*cf.* § 374); the hardness is increased (*cf.* §§ 367, 458, 464, and 470). Copper containing 0.8% of arsenic has only 30% of the electric conductivity of pure copper.

404. Classification of the Metals. — The metals may be classified and studied according to several systems. One of these systems is that of “**Qualitative Analysis**,” a branch of Chemistry in which we identify the common metals and acid radicals present in a mixture.

The Qualitative scheme is based upon the properties of the *sulphides* (*cf.* § 255). These may be classified as, —

(1) **soluble**, including sulphides of Groups I and II (see below);

(2) **moderately insoluble**: sulphides of Groups III and IV;

(3) **very insoluble**: sulphides of Groups V and VI. The

Qualitative grouping is as follows: —

Group I.	Group II.	Group III.	Group IV.	Group V.		Group VI.
				Div. I.	Div. II.	
Na.	Mg.	Al.	Fe ^{II} .	Ag.	Hg ^{II} .	As.
K.	Ca.	Cr.	Co.	Hg ^I .	Pb.	Sb.
NH ₄ .	Sr.	Fe ^{III} .	Ni.	Pb.	Bi.	Sn.
	Ba.		Mn.		Cu.	Pt.
			Zn.		Cd.	Au.

The order in which the metals are studied in Chapters XXX to XXXVII, inclusive, is determined, in general, by the Periodic system. Arsenic, antimony, and bismuth have been given under the nitrogen family (Chap. XXVI).

1. **Alkali Metals.** — The alkali metals include *sodium*, *potassium*, and the radical, *ammonium*; also the rare metals, lithium, rubidium, and caesium. The valence of these metals is **I**, their oxides and hydroxides form strong bases, and their salts with strong acids are neutral.

2. **Alkali-Earth Metals.** — The common alkali-earth metals are *magnesium*, *calcium*, *strontium*, and *barium*. Glucinum and **radium** belong in this family. All these metals are **bivalent**, their oxides and hydroxides are strong bases, and their salts with strong acids are neutral.

3. **Zinc, Cadmium, and Mercury.** — These form a sub-group of periodic group II. Zinc and cadmium are bivalent, but mercury is both univalent and bivalent. The oxides and hydroxides are feeble bases.

4. **Copper, Silver, and Gold.** — Although classified with the alkali metals in the periodic table, copper, silver, and gold differ from them. Silver is commonly univalent, copper bivalent, and gold trivalent.

5. **Aluminum.** — Aluminum is trivalent, and forms a hydroxide that is both an acid and a base.

6. **Iron, Cobalt, and Nickel.** — The hydroxides of these metals are feeble bases. The compounds are of two series: "ous" and "ic," in which the metal is bivalent and trivalent, respectively.

7. **Manganese.** — Manganous salts are derived from the oxide MnO . The acid properties of the oxides increase with the increasing per cent of oxygen. Mn_2O_7 is the anhydride of permanganic acid.

8. **Chromium.** — The oxide Cr_2O_3 is basic, giving chromic salts; but CrO_3 is the anhydride of chromic acid.

9. **Tin and Lead.** — These belong to the carbon family. The oxides and hydroxides in which the valence of the metal is 2 are both weak bases and weak acids. Those in which it is 4 are stronger acids, giving *stannates* and *plumbates*.

10. **Platinum.** — The platinum and palladium divisions of periodic group VIII, together with *gold*, *silver*, and *mercury*, are called **noble metals**. The others are **base metals**. The noble metals are chemically inactive, and their oxides and salts are decomposed by heat.

405. Electromotive Series. — In the electromotive series of the metals (*cf.* § 180 and **Appendix x**) we have an arrangement in which the metals coming first displace those that follow, from solutions of their salts. The series represents much more than this. Thus, the metals coming first are active, and form stable oxides. Their hydroxides are strong bases. The metals at the end of the series ("noble" metals) are inactive, and form unstable oxides. Since their oxides are unstable, metals like gold and platinum occur free, while potassium, etc., do not. The oxides

from gold to mercury, inclusive, are decomposed by heat; those from arsenic to manganese are reduced by hydrogen and carbon; while those above manganese are neither decomposed by heat nor readily reduced. Naturally, the metals coming first in the series were the last to be discovered and prepared by man.

406. Compounds of the Metals. — The compounds of the metals are classified as **oxides, hydroxides, and salts**. Oxides and hydroxides of metals are *bases* in the presence of water. Salts may be *normal, acid, or basic* (cf. §§ 163 to 165).

Oxides of metals are nearly all *insoluble*. Some, however, react with water to give *soluble hydroxides*. Oxides may be made by the oxidation of metals (cf. § 24), and by the decomposition of hydroxides, carbonates, nitrates, etc., by heat.

Hydroxides of the alkali metals and of the alkali-earth metals, except magnesium, are soluble. *All other hydroxides are insoluble*. Hydroxides are made by the union of oxides and water (cf. § 161), or by double decomposition (cf. §§ 459 and 476).

Salts are made by, —

- (1) Union of metals and non-metals (cf. § 118);
- (2) Reaction between metals and acids (cf. § 47);
- (3) Neutralization.
- (4) Reaction between an acid and the salt of a volatile acid (cf. § 126);
- (5) Reaction between a base and the salt of a volatile base (cf. § 203);
- (6) Double decomposition between salts.

The occurrence of **sulphides**, their preparation, and their properties are given in §§ 253 to 255, and in § 404 (*q. v.*).

Chlorides, bromides, and iodides are made by the general methods of making salts. In many cases the anhydrous substance can be prepared only in the absence of water, since evaporation of the aqueous solution causes hydrolysis (*cf.* § 441). Practically all halides are soluble except those of lead, silver, and mercury (**ous**).

Nitrates are *soluble*, although some, *e. g.*, $\text{Bi}(\text{NO}_3)_3$, are hydrolyzed. All are decomposed by heat (*cf.* § 230).

Nitrites are also soluble. They are decomposed by strong acids, giving nitrogen oxides (*cf.* § 234).

Sulphites are normal or acid (*cf.* § 259). The normal sulphites of the alkali metals are soluble; other normal sulphites are insoluble. Most acid sulphites are soluble. All sulphites are decomposed by strong acids.

Sulphates are formed by the general methods; some by the oxidation of sulphides, *e. g.*, $\text{CuS} + 2 \text{O}_2 \longrightarrow \text{CuSO}_4$. All sulphates are soluble except those of lead, barium, and strontium.

Carbonates are *insoluble*, except those of the alkali metals. Since carbonic acid is weak, its salts with weak bases are completely hydrolyzed in the presence of water.



All carbonates are decomposed by acids, giving carbon dioxide. All are readily decomposed by heat, except those of the alkali metals, of barium, and of strontium.

Phosphates (normal) are *insoluble*, except those of the alkali metals. The common soluble phosphates are *primary* or *secondary* (*cf.* § 357). Those produced by precipitation are generally tertiary (**normal**) orthophosphates.

Silicates of the alkali metals are soluble; others, insoluble. All are decomposed by acids, giving silicic acid. In the metaphosphate or borax bead silicates are insoluble, and form a "silica skeleton."

407. Exercises.

1. Classify the metals of the Qualitative groups into "light" and "heavy" metals.
2. Enumerate the alloys described in this book, and give the uses of each.
3. If you had a solution containing a mixture of the nitrates of all the metals of the Qualitative grouping, how could you separate the metals of Div. I, Group V, from all the others? How could you separate barium, lead, and strontium from all the others? How separate Groups I and II from all the others?
4. What difference would there be between the action of sodium hydroxide upon aluminum hydroxide and its action upon magnesium hydroxide? Why?
5. Why would the metals at the bottom of the electromotive series naturally be discovered first? When primitive man abandoned stone as the material of his tools, weapons, etc., what metal might he be expected to find that possessed the necessary properties, and was sufficiently abundant for his use? Why would he not use iron at once? What metals made up "bronze"? What was the "Bronze Age"?

CHAPTER XXX.

THE ALKALI METALS.

408. General Properties. — The metals, like the non-metals, are generally studied in groups or natural families based upon similarity of properties. The **Alkali** group consists of the *five* metals named below and the *radical* ammonium, NH_4 , the compounds of which resemble those of sodium and potassium (*cf.* § 210). These metals are called “alkali” metals because the two most important members of the group are contained in the *alkalies*, i. e., in sodium and potassium hydroxides.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	SPECIFIC GRAVITY.	MELTING POINT.
Lithium.	Li	7	0.59	180° C.
Sodium.	Na	23	0.97	95.6° C.
Potassium.	K	39	0.87	62.5° C.
Rubidium.	Rb	85.4	1.52	38.5° C.
Cæsium.	Cs	133	1.85	26.5° C.

All of these metals have a silvery white luster and are easily cut. In air they become coated with a layer

of the *oxide* and the *hydroxide*; if *carbon dioxide* is present, these pass into the corresponding *carbonates*. The alkali metals burn when heated in air, and decompose water at ordinary temperatures; therefore none of them is found *free* in nature. The salts of these metals are practically all soluble in water.

The properties of the alkali metals change in the order of the atomic weights, *e. g.*, the higher the atomic weight the lower the melting-point. The chemical activity and the electro-positive character *increase* from *lithium* to *cæsium*. Cæsium is the most electro-positive element known.

409. Lithium. — Lithium is widely distributed in nature, but no mineral known contains a large proportion of it. It is found in *minute* quantities in most mineral waters, in many plants, and in the blood. Lithium is the lightest of the metals. Its salts color the Bunsen flame *crimson*.

410. Sodium. — Sodium occurs widely distributed and in large quantities, especially as *sodium chloride*, NaCl. This exists as *rock-salt* and *sea-salt*, and in many mineral springs. *Sodium silicate* is found in many rocks; the *nitrate* is Chili saltpeter. Large deposits of the sulphate and carbonate exist. The ashes of plants growing in or near the sea contain sodium carbonate, and were formerly the source of many sodium compounds.

Sodium is prepared by the *electrolysis of melted sodium hydroxide* (Fig. 81). This is **Castner's process**. The resistance of

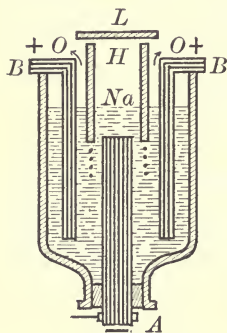


FIG. 81.

the hydroxide generates the heat that keeps it melted, after the operation has begun. The vessel containing the hydroxide is of iron, and the **anode** (*BB*) is either a cylindrical iron or nickel vessel, or a number of pieces of gas carbon. The **cathode** (*A*), extending up into the hydroxide, is of iron or carbon. When the current passes, globules of sodium collect upon the cathode, and rise to the top at *Na*. They accumulate in the collecting cylinder (*Na, H*) which floats on the melted hydroxide, just over the cathode.

The lower part of the collecting cylinder consists of wire gauze (shown by dots), which prevents the globules of sodium from going to either side. The *anion* (OH^-) gives water and oxygen at the anode: —



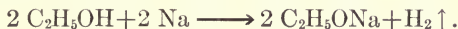
Electrolysis of some of the water gives hydrogen at the cathode and more oxygen at the anode. The hydrogen accumulates with the sodium in the collecting cylinder (*Na, H*), and protects the sodium from the air (*cf.* § 54). The melted sodium is removed by means of ladles, while the hydrogen escapes under the cover (*L*). The oxygen (*O*) is conducted away with great care, to prevent its coming in contact with the other products.

411. Properties of Sodium. — Sodium is a white metal, so soft at ordinary temperatures that it can

be molded between the fingers, or pressed into wire. At -20° C. it is quite *hard*. It has the characteristic properties of the metals, including conductance for heat and electricity (*cf.* §§ 74, 401, and 408). The molecule is **monatomic** (*cf.* § 142); so is that of potassium.

Sodium burns in air or oxygen with a bright, yellow flame. The same characteristic color is imparted to a non-luminous flame by any sodium compound, and serves as a **test** for the element.

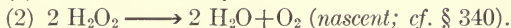
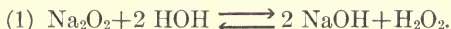
Sodium burns energetically in *chlorine* (*cf.* § 118) and in sulphur vapor. It acts upon alcohol much as upon water, forming *sodium ethylate* and hydrogen (*cf.* § 220).



It does not react with ether, nor with the liquid hydrocarbons, and is usually kept under *ligroin* or kerosene (*cf.* § 525). When exposed to ordinary air it is soon converted into the carbonate.

An *alloy* of sodium and mercury, called **sodium amalgam** (*cf.* § 403), is an important *reducing agent*; it is *diluted* sodium.

When sodium is burned in air or oxygen, the product is a mixture of the *monoxide* (Na_2O) and the *peroxide* (Na_2O_2). The **peroxide** is the sodium salt of hydrogen peroxide (*cf.* § 339). It is a powerful oxidizing and bleaching agent.



The **monoxide** is made by beating sodium nitrate or hydroxide with sodium, in the absence of air.



412. Sodium Hydroxide. — Sodium hydroxide, or *caustic soda*, is formed when sodium or its oxides react with water. The **commercial methods** of preparing it are:—

(1) Boiling a solution of *sodium carbonate* with *slaked lime* (calcium hydroxide).

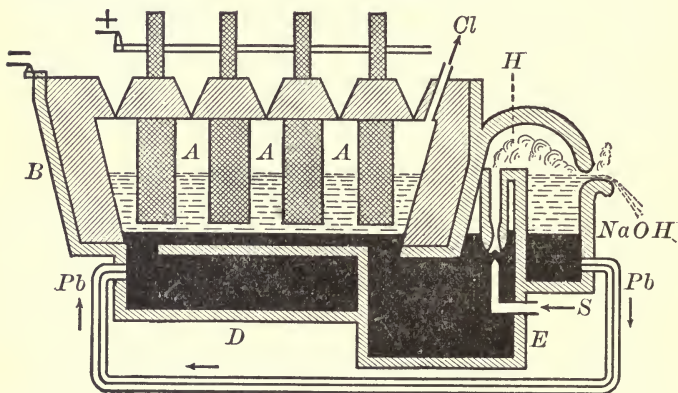
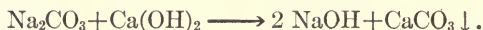
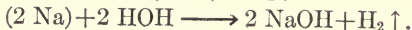
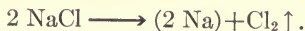


FIG. 82.

The calcium carbonate is precipitated. The sodium hydroxide solution is drawn off and evaporated.

(2) Electrolysis of *aqueous sodium chloride* (**Castner's process**).



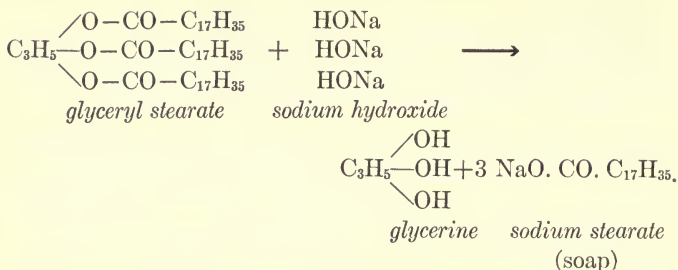
The last two products collect at the cathode.

(3) Electrolysis of **fused** sodium chloride (**Acker** process). The apparatus is shown in Fig. 82.

The carbon anodes (*A, A, A*) dip into fused sodium chloride. This floats upon **melted lead** (solid black of figure), which is in contact with the cast-iron box (*B*), and forms the cathode. The sodium forms an alloy with the lead, while the chlorine is carried away at *Cl*, to be converted into bleaching powder. The sodium-lead alloy passes into compartment *E*, in which a jet of steam (*S*) forces the alloy over into *H*. At the same time the steam reacts with the alloy, forming lead, sodium hydroxide and hydrogen. The hydrogen burns. The melted lead collects *under* the sodium hydroxide, and is returned through the pipe *Pb* to compartment *D*. The sodium hydroxide is transferred to metal "drums," which form the commercial packages.

Sodium hydroxide is a white, deliquescent solid, very soluble in water. The solid is used as a drying agent (*cf.* § 203). Both the solid and its solution absorb carbon dioxide readily. Sodium hydroxide is one of the strongest and most useful bases. Enormous quantities of it are used in "softening" water, in making soap, and in various chemical industries (*cf.* § 525).

413. Soap. — When fats are boiled with alkalies, they are *saponified*, *i. e.*, converted into soap. Thus "stearin," which is *glyceryl stearate* (*cf.* § 540), and caustic soda give *sodium stearate* and *glycerine*. The sodium salt of the organic acid (here, *stearic acid*) is **soap**.

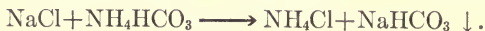


The sodium stearate formed is "salted out" of solution by adding sodium chloride.

When soap is dissolved in water it is partly *hydrolyzed* (cf. § 184) into sodium hydroxide and the organic acid; the sodium hydroxide is the cleansing agent. When soap is put into *hard* water, an insoluble scum is formed; this is the *calcium* salt of the organic acid.

414. Sodium Carbonate. — Sodium carbonate, or *soda*, is one of the most important chemicals manufactured. The principal methods of making it are the **Solvay**, or *Ammonia*, **Process** and the **Le Blanc Process**. The second of these is the more interesting *historically*, because it was devised by Le Blanc for the French government during the Revolution, when the supply was cut off; but the ammonia process is so much cheaper that fully three-fourths of the soda used is now made in this way. Both processes begin with common salt.

The **Solvay Process** consists essentially in treating *sodium chloride* with *ammonium hydrogen carbonate*, NH_4HCO_3 .



This reaction takes place because sodium hydrogen carbonate (*sodium bicarbonate*) is not very soluble in water and is, therefore, readily precipitated when *ammonium hydrogen carbonate* is added to concentrated salt solution. The solution of ammonium hydrogen carbonate is formed by passing carbon dioxide under pressure into a saturated solution of ammonia (NH_4OH).



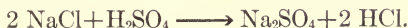
Gentle heating converts the bicarbonate into carbonate.



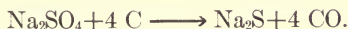
The carbon dioxide thus set free is used again; and nearly all the ammonia is recovered by heating the brine, from which the bicarbonate has crystallized, with slaked lime (*cf.* § 203).

The **Le Blanc Process** consists of essentially *three* operations:—

(1) The conversion of common salt into *sodium sulphate* (*cf.* § 126);



(2) The reduction of sodium *sulphate* to sodium *sulphide*;



(3) The conversion of sodium sulphide into the *carbonate*;



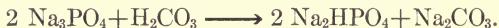
The *second* and *third* operations take place *together*, sodium sulphate being mixed with limestone and coal-dust and the mixture heated. The sodium carbonate cannot readily be separated from calcium sulphide because both are soluble. If limestone is present *in excess*, however, some of it is dissociated into quicklime (CaO) and carbon dioxide; the quicklime and the calcium sulphide form an insoluble compound.

Soda comes into the market as *calcined soda*, or *soda-ash*, containing no crystal water, and as *crystallized soda* or *sal sodae*, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$. Soda is used in great quantities in the manufacture of *glass* (cf. § 394) and of *sodium hydroxide* (§ 412), and to soften water.

415. Sodium Bicarbonate. — Sodium bicarbonate is prepared by treating the normal salt with carbonic acid (cf. § 284). The equation for its decomposition by heat is given in § 414. It is used in large amounts for baking powders, effervescing mixtures, “soda-water,” and medicine.

416. Sodium Phosphate. — The common phosphate of sodium is *disodium hydrogen phosphate*, $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$; it is formed by adding sodium carbonate to phosphoric acid until the solution is slightly *alkaline*.

Phosphoric acid is *tribasic* (cf. § 355) and its *insoluble* salts are usually *normal*, e. g., Li_3PO_4 , $\text{Ca}_3(\text{PO}_4)_2$, Ag_3PO_4 ; but its normal sodium salt (Na_3PO_4) is so readily *hydrolyzed* (cf. § 357) that it absorbs carbonic acid from the air.



417. Sodium Chloride. — Sodium chloride, or *common salt*, occurs widely distributed. It makes up about 3% of sea-water, and is found in large deposits in Galicia (Austria), Germany, England, the United States, etc. In some places salt is mined as *rock-salt*,

while in others the mixture of salt and earth is treated with water, the resulting brine being pumped to the surface and then evaporated. In modern plants the brine is concentrated and the salt continuously separated in a " vacuum " boiler.

Sodium chloride crystallizes in colorless, transparent *cubes*, which *décrepitate* (*cf.* § 88) when heated. It is only a little more soluble in hot than in cold water (*cf.* § 80).

Salt is necessary to the life of man and other animals, the hydrochloric acid of the gastric juice being derived from it (*cf.* § 125). It is used in enormous quantities, not only as food, but as the *starting material* in the preparation of most compounds of *sodium* and of *chlorine*.

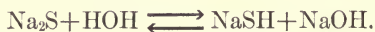
418. Sodium Nitrate. — Sodium nitrate occurs as Chili saltpeter (*cf.* § 231). It is somewhat deliquescent, hence it cannot be used for the better grades of gunpowder. It is converted into potassium nitrate, which is *not* deliquescent, and into nitric acid (*cf.* § 223). Sodium nitrate is also used as a fertilizer (*cf.* § 358). The crude salt is an important source of *iodine* (*cf.* § 323).

419. Other Sodium Salts. — Sodium sulphate is made (in two stages) from salt and sulphuric acid (*cf.* § 126). The acid salt (NaHSO_4) is first formed. The normal salt, i. e. its *hydrate*, is formed from salt and magnesium sulphate solutions.



"**Glauber's Salt**" is the *decahydrate*, $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$. It effloresces completely in dry air. The principal use of sodium sulphate is as a substitute for soda in glass-making.

Sodium sulphide, Na_2S , is prepared by the "neutralization" method (§ 254); also by the *reduction* of the sulphate. It forms large, deliquescent crystals. In solution it is hydrolyzed, giving the *hydrosulphide* and the *hydroxide*. Other **soluble** sulphides behave in the same way.



Sodium sulphide unites with sulphur, forming **polysulphides**, Na_2S_2 , Na_2S_3 , etc. Potassium and ammonium sulphides do the same (*cf.* § 427).

Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$) is described in § 268; **sodium tetraborate** ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$), or *borax*, in § 399.

Sodium cyanide, NaCN , is a soluble, white solid, used in the "*cyanide process*" to extract gold from poor ores (*cf.* § 468). It is made for this purpose by the reaction between *ammonia gas*, *sodium*, and *carbon*. It resembles potassium cyanide (*q. v.*).

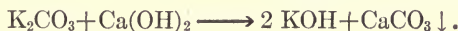
420. Potassium. — Potassium is a constituent of many rocks, such as *potash feldspar* and *mica* (*cf.* § 472), and by their disintegration becomes a part of the soil. Plants require potassium salts for their growth (*cf.* § 358), and potassium carbonate (*potash*) is found in plant ashes. The residues left after sugar is extracted from beets (§ 543), the **argols** of wine casks (*cf.* § 538), and **suint**, a substance obtained in the washing of sheep's wool, all contain potassium salts. When these (and other) potassium salts of organic acids are burned, potash is left.

The most important source of potassium compounds at present are the deposits at Stassfurt, near Magdeburg, Germany. Here, on top of a layer of salt about 4,000 feet in thickness, are layers about 90 feet thick, which contain potassium salts, either alone, or as "double salts" of potassium with magnesium salts, calcium salts, etc. Some of these salts are: *sylvite* (KCl), *carnallite* (KCl, MgCl₂, 6 H₂O), *kainite* (MgSO₄, MgCl₂, K₂SO₄, 6 H₂O), and *polyhalite* (K₂SO₄, MgSO₄, 2 CaSO₄, 2 H₂O). By very exact methods of solution and recrystallization the potassium salts are separated from the others.

Potassium is made by the electrolysis of either potassium chloride or the hydroxide (*cf.* § 410). It is a soft metal, like sodium, but has a slightly bluish luster. Like sodium, it must be kept under *kerosene* or *ligroin*. When exposed to the air, and when burned, it gives the oxide K₂O₄. The oxide, K₂O, is similar to Na₂O, and is made by similar methods (*cf.* § 411). Potassium decomposes water energetically (*cf.* § 74). It is not used to any great extent, since sodium, which is much cheaper, can be used instead.

The vapors of potassium and its salts color the non-luminous flame violet.

421. Potassium Hydroxide. — Potassium hydroxide, or *caustic potash*, is made by the electrolysis of potassium chloride. The method resembles that for the preparation of caustic soda (*cf.* § 412). It is also made from potassium carbonate by treatment with "milk of lime," i. e., *calcium hydroxide*.



Potassium hydroxide is a white, deliquescent solid which unites readily with the water and carbon dioxide of the air. It is used as a drying agent. It is a powerful base, saponifying fats as caustic soda does. Potassium salts of stearic, etc., acids (*cf.* § 413) form "soft soap."

422. Potassium Carbonate. — Potassium carbonate is made by the Le Blanc process from potassium chloride (*cf.* § 414). The crude substance is obtained when potassium salts of organic acids are decomposed, as by burning (*cf.* § 420). It is, therefore, present in *wood-ashes*. The anhydrous substance is a powerful *dehydrating* agent.

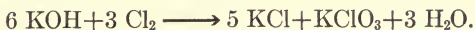
Potash is used to make the *hydroxide* and *hard glass*.

In chemical analysis, a solid insoluble in acids is converted into soluble substances by fusing it with a mixture of potassium and sodium carbonates. The mixture has a lower melting point than either carbonate alone. Only *one* of the carbonates need be given in the equation. *Barium sulphate* reacts thus: —



If the mixture obtained by fusion is heated with water, the SO_4 is dissolved (as K_2SO_4), and may be tested for. The residue, insoluble in water, contains the Ba (as BaCO_3). Dilute nitric acid converts it into Ba^{++} , *i. e.*, $\text{Ba}(\text{NO}_3)_2$. When, therefore, an insoluble salt is fused with the two alkali carbonates, the *acid radical* is in the part *soluble* in water, while the metal is in the *insoluble* part, either as *carbonate*, or as *oxide* or *free metal*, if the carbonate is unstable.

423. Potassium Chlorate. — Potassium chlorate results when chlorine is passed into a *hot*, concentrated solution of potassium hydroxide until the solution is saturated (*cf.* § 331).



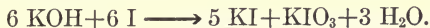
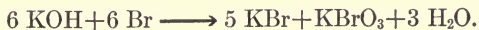
A cheaper way is to pass the chlorine into *hot* "milk of lime"; calcium chlorate, $\text{Ca}(\text{ClO}_3)_2$, is formed. This with *potassium chloride* gives *potassium chlorate* and *calcium chloride*.



Potassium chlorate, being much less soluble in cold water than the other substances, *crystallizes out*, leaving the others in solution.

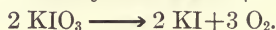
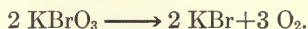
Like the nitrate, potassium chlorate is valuable chiefly as an oxidizing agent. It is used in preparing oxygen, explosive mixtures, e. g., *smokeless powder*, matches, and fireworks. It is sold by druggists as "potash" for sore throats.

424. Potassium Bromide (KBr) and Potassium Iodide (KI). — Potassium bromide and potassium iodide may be prepared by the action of *bromine* and *iodine*, respectively, upon potassium hydroxide. The equations are analogous to the one for the action of *chlorine* upon caustic potash.

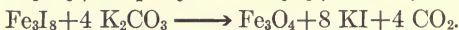
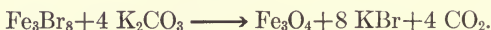


By evaporating the solution containing *bromide* and *bromate*, or *iodide* and *iodate*, to dryness, and then heating the residue

sufficiently, we can decompose the bromate and the iodate just as we can the chlorate (*cf.* § 19).



Potassium bromide and iodide are made, also, by treating the bromide and the iodide of iron with potassium carbonate.



The iron compounds are formed by adding bromine and iodine, respectively, to moist iron turnings.

425. Potassium Sulphates.

When potassium chloride, nitrate, acetate, etc., are treated with concentrated sulphuric acid, the *acid sulphate*, or *bisulphate*, KHSO_4 , is the first, and usual, product, as is the case with sodium salts (*cf.* §§ 126 and 224). The acid sulphate is also formed from the sulphate and concentrated sulphuric acid (*cf.* §§ 164 and 267). It forms large crystals which melt readily, and give off water, leaving the *pyrosulphate* (*cf.* § 260).

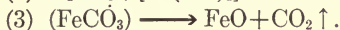
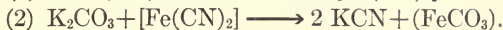
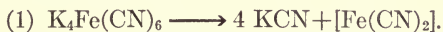
Normal potassium sulphate (K_2SO_4) is made from the acid sulphate and the chloride, etc., at red heat (*cf.* § 126); also by *neutralizing* the hydroxide or carbonate with dilute sulphuric acid. It crystallizes from water without water of hydration, and, except for decrepitation, is stable when heated. The salt is found in the Stassfurt deposits (*cf.* § 420). It is used as a fertilizer, and to prepare potassium carbonate by the Le Blanc process.

426. Other Potassium Salts.

Potassium nitrate has been described in §§ 230 to 232. It is made by the double decomposition of hot, saturated solutions

of *potassium chloride* and *sodium nitrate*. When it is heated it melts and loses one third of its oxygen, giving the **nitrite** KNO_2 , (cf. § 234). This is a soluble, white, crystalline solid.

Potassium cyanide (KCN) is a white, deliquescent solid, very soluble in water. The solution is very alkaline, owing to hydrolysis. Exposed to air, the cyanide is converted into carbonate and *prussic acid* (cf. § 290). It is very poisonous. It is used to prepare **electroplating** solutions (cf. § 464), to extract gold from its ores (cf. §§ 419 and 468), and as a reagent. Potassium cyanide is made by heating a mixture of *potassium ferrocyanide* (cf. § 496) with *potassium carbonate*.



Potassium thiocyanate (KSCN) is a soluble, white crystalline solid, used in the laboratory to detect *ferric* salts.

Potassium hydrogen tartrate ($\text{KHC}_4\text{H}_4\text{O}_6$) is also called *potassium bitartrate*, *potassium acid tartrate*, and “cream of tartar” (cf. § 280). It is a white, crystalline solid, requiring 253 times its weight of water, at 10°C ., to dissolve it. The corresponding sodium salt is very soluble.

427. Ammonium Salts. — The formation of ammonium salts by the neutralization of acids by ammonia water is described in § 210. The radical NH_4 has not been isolated, because it breaks up into *ammonia* and *hydrogen*. Most ammonium salts are white, soluble solids, which, except for their instability, resemble the corresponding potassium compounds.

Ammonium amalgam is a bulky, metallic substance resembling *sodium amalgam* (cf. § 411). It is formed when sodium

amalgam reacts with a concentrated solution of ammonium chloride.



Ammonium amalgam breaks up into *ammonia*, *hydrogen*, and *mercury*.

Ammonium chloride is used in soldering, in making galvanized iron (*cf.* § 448), and for “sal ammoniac” batteries, as well as in the preparation of ammonia and as a reagent in the laboratory.

Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, is an important fertilizer.

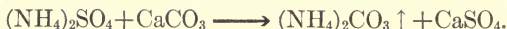
Ammonium nitrate, NH_4NO_3 , is a white, deliquescent solid (*cf.* § 85). It is used in preparing *nitrous oxide* (*cf.* § 238).

Ammonium hydrogen tartrate, $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$, is difficultly soluble, like the corresponding potassium salt.

Ammonium phosphate is $(\text{NH}_4)_2\text{HPO}_4$. Like the corresponding sodium salt, it is used as a source of PO_4 in the laboratory.

Ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, is a source of oxalate ions, C_2O_4 .

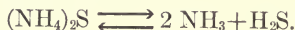
Ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, is used for the carbonate ions of its solution. The commercial salt is made by heating ammonium sulphate with calcium carbonate. The ammonium carbonate *sublimes* (*cf.* § 211).



The product is not pure $(\text{NH}_4)_2\text{CO}_3$, but contains NH_4HCO_3 and *ammonium carbamate*, $\text{NH}_2\text{COONH}_4$. When the solution of the impure salt is treated with carbon dioxide, it gives the pure salt as a precipitate. Ammonium carbonate breaks up readily into *ammonia*, *carbon dioxide*, and *water*. For this reason it is used in some baking powders. As “solid ammonia” it is used for smelling salts and as a water softener.

Ammonium sulphide, $(\text{NH}_4)_2\text{S}$, is made as stated in § 254.

It is a common source of sulphide ions (S) in the laboratory. The substance is readily dissociated: —



The hydrogen sulphide is oxidized by the air, and sulphur is liberated. This unites with the unchanged ammonium sulphide to give **yellow** ammonium sulphide, which is $(\text{NH}_4)_2\text{S}$, $(\text{NH}_4)_2\text{S}_2$, etc. The same substance is formed from "colorless" ammonium sulphide and sulphur.

Ammonium salts are used so generally in the laboratory because they are soluble, and, further, because they can be removed at any time from a mixture, owing to the ease with which they are dissociated into volatile materials. The test for ammonium salts is that they all react with lime, giving *ammonia*.

428. Exercises.

1. If the molecule of sodium is monatomic (*cf.* § 411), how does the weight of a liter of its vapor compare with that of a liter of oxygen under the same conditions? Answer the same question for potassium.

2. What products would be formed at each electrode in the electrolysis of ammonium chloride? Of ammonium nitrate?

3. How would you prepare *sodium chlorate*, *ammonium hydrogen carbonate*, *sodium potassium tartrate*, *potassium silicate*, *potassium oxalate*, *ammonium mono-hydrogen phosphate*?

4. Write the equations showing the preparation of potassium carbonate by the Le Blanc process.

5. All four substances in the equation of § 419 are *soluble*. Under what conditions can the reaction take place?

6. Which of the following gases would you dry with solid caustic potash: *ammonia*, *chlorine*, *hydrogen sulphide*, *carbon monoxide*, *carbon dioxide*, *oxygen*, *hydrogen*? What reactions would take place with the others?

7. How would you distinguish an *ammonium* salt from one of potassium or sodium? How distinguish between a potassium salt and a sodium salt?

CHAPTER XXXI.

THE ALKALINE-EARTH METALS.

429. The Group. — The “alkaline-earth” metals (also called the “*calcium family*”) form a part of the **second periodic group**, and are intermediate between the alkali metals and the “earth” metals, such as

Element.	Mg.	Ca.	Sr.	Ba.
Atomic Weight.	24	40	88	137
Specific Gravity.	1.75	1.85	2.5	3.78
Metal melts.	633° C.	760°	800°	850°
Carbonate dissociates.	300° C.	600°	1100°	1500°
Grams of Hydroxide Soluble in 1 l. H ₂ O at 18° C.	0.01	1.7	7.7	37
Heat of Formation of Chloride, in Calories.	151	170	185	195
Grams of Sulphate Soluble in 1 l. H ₂ O.	354	2.07	0.107	0.0027

aluminum. The group consists of *calcium*, *strontium*, and *barium*. While *magnesium* really belongs with the metals glucinum, zinc, cadmium, and mercury, in a separate division of Group II, yet many of its properties ally it with the calcium group, and we

include it with them in this chapter. The metal **radium** also belongs in this group. Magnesium reacts with water at $100^{\circ}\text{C}.$; the others even at the ordinary temperature. The hydroxides of these metals are strong bases, and their salts with strong acids are *neutral*. The table shows that the properties of the members of the group and of their compounds, *vary in the order of the atomic weights*.

430. Calcium. — Calcium does not occur free, but its compounds are found in large quantities. The most abundant is the *carbonate*, CaCO_3 ; this occurs as *limestone*, *marble*, *chalk*, *calc-spar*, and *coral*. The *sulphate*, CaSO_4 , the *phosphate*, $\text{Ca}_3(\text{PO}_4)_2$, and the *fluoride*, CaF_2 , are also important minerals.

Calcium is a crystalline solid with a white, metallic luster. It is a little harder than lead. With water it reacts as sodium does, but less vigorously. Beyond being covered with a thin film of oxide, it does not react with dry air at the ordinary temperature. At $760^{\circ}\text{C}.$, its melting temperature, it takes fire, giving a mixture of CaO and Ca_3N_2 .

Calcium is obtained by the **electrolysis of fused calcium chloride** (Fig. 83). The vessel holding the chloride is of carbon, and forms the anode. The calcium chloride at the bottom of the

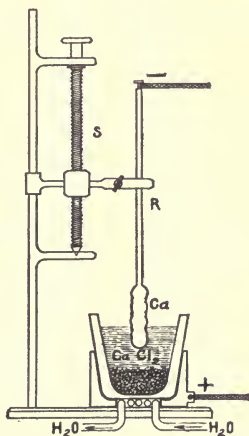
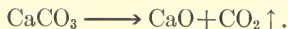


FIG. 83.

anode is kept cold and solid by flowing water. That above is kept liquid (it melts at 719°C.) by the resistance of the current. The cathode is a copper or iron rod (R), which dips into the melted calcium chloride. As the calcium is liberated, it rises to the top, and collects on the cathode. The cathode is raised by the screw (S), so that the accumulated metal is gradually raised out of the melted bath. Sticks several feet long are thus obtained. Calcium is not used for dehydrating alcohol because it reacts with the alcohol as well as with the water. The calcium hydroxide and alcoholate formed are insoluble in the alcohol.

431. Calcium Oxide.—Calcium oxide (*lime*, or *quicklime*) is made by heating calcium carbonate, *e. g.*, *limestone*, above 600°C.



If carried out in a closed vessel, the reaction is **reversible** (*cf.* § 243). On a commercial scale, the limestone is heated in a large furnace, called a **lime-kiln** (Fig. 84).

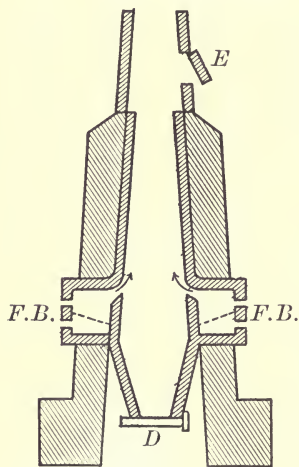


FIG. 84.

The construction of a modern lime-kiln is shown in the figure. It consists of a long shaft of brick or limestone blocks, and is charged with limestone from the top (E). A number of *fire-boxes* ($F. B.$) are built around the lower part of the shaft, and the hot gases from the fires enter the shaft, and cause the dissociation of the limestone. This is the "*long-flame*" process. The effi-

ciency of the operation depends on the removal of the carbon dioxide as rapidly as it is formed. In this way the *reverse action* is prevented. The lime is removed at the bottom (D).

Lime is a white, amorphous solid, fusible only at the temperature of the electric furnace. It is used in the lime light (§ 55). When treated with water, it gives "**slaked lime**," a soft, dry powder. The reaction is a **reversible** one: —



Much heat is evolved in slaking lime. As a result, leaky cars and warehouses containing it are often set on fire. Lime is used to remove water and carbon dioxide from gases (*cf.* § 297). When exposed to the air, it forms *air-slaked* lime, a mixture of the hydroxide and carbonate.

432. Calcium Hydroxide. — Calcium hydroxide is not very soluble (*cf.* § 429, Table). The solution is *lime-water*. "**Milk of lime**" is lime-water with undissolved calcium hydroxide.

Uses. — Lime is generally slaked just before it is used. Some uses are: to prepare *ammonia* (*cf.* § 203), the *hydroxides* of sodium and potassium (*cf.* §§ 412 and 421), *bleaching powder* (*cf.* §§ 122 and 438), *chlorates* (*cf.* § 331), *glass*, *mortar*, and *cement* (*cf.* § 436); to purify sugar and illuminating gas (*cf.* § 297); to remove hair from hides; to *soften water* (*cf.* § 435); to extract metals from their ores; as a *disinfectant* and *white-wash*, and in the making of candles.

433. Calcium Chloride (CaCl₂). — Calcium chloride is usually made from *calcium carbonate* and *hydrochloric acid* (*cf.* § 277). The *anhydrous* substance (made by heating at 200° C.) is very *deliquescent*, and dissolves in water with evolution of heat. It is used as a *drying agent* (*cf.* § 90).

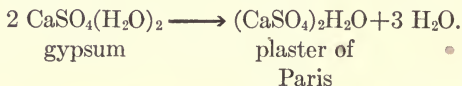
The hydrate, $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$, *absorbs* heat when dissolving in water (cf. § 88), and when mixed with ice or snow may produce a temperature of -48°C . A concentrated solution of calcium chloride freezes so much lower than one of sodium chloride that it is often used instead of brine as the cold bath in ice factories (cf. § 207).

434. Calcium Carbonate (CaCO_3). — As already stated (cf. § 285) calcium carbonate occurs in many forms and widely distributed. *Limestone*, *chalk*, *calcite*, and *marble* are found in large masses. *Aragonite* crystallizes in a form different from that of the other varieties, but has the same composition.

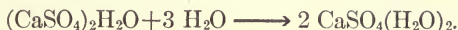
Limestone, the most abundant form of calcium carbonate, is *gray*, and often contains small crystals, but is always mixed with clay and other impurities. Limestone containing much clay is **marl**. Marl is used in making cement. Limestone is used as a *flux* (cf. § 482) in smelting iron, as a source of *lime*, and as building-stone. **Chalk** is used for making lime. Carpenters use it for *marking*. **Marble** is used for building purposes, as a source of lime, etc.

435. Calcium Sulphate (CaSO_4). — Calcium sulphate occurs principally as *gypsum*, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$. *Alabaster* is a granular form of gypsum. *Crayon* contains gypsum.

When gypsum is heated to 120° to 130°C . it loses about *three-fourths* of its crystal water, and forms the white powder known as **Plaster of Paris**.

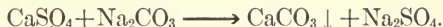


When this powder is mixed with enough water to form a paste it expands, and hardens to a mass with a smooth surface. Because of these properties plaster of Paris is used to make *casts*, *rigid* surgical bandages, as a wall finish, and as a cement. The union of the powder with water produces the crystalline compound.

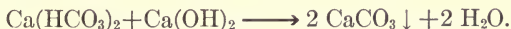


Stucco consists of plaster of Paris, stone, and glue.

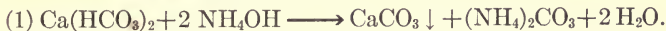
Softening of Water. Calcium sulphate is slightly soluble; water containing it is **permanently hard** (*cf.* § 70). Permanent hardness may also be due to *magnesium* sulphate or chloride, calcium chloride, etc. If water contains only **permanent** hardness, the softening, or "breaking," may be accomplished by the use of a soluble carbonate, such as Na_2CO_3 or $(\text{NH}_4)_2\text{CO}_3$ (*cf.* §§ 414 and 427).



If the water contains only *temporary* hardness, it may be "broken" by boiling (*cf.* § 284), or by means of the theoretical amount of *lime*.



If the water contains **both** kinds of hardness, NaOH or NH_4OH may be used. This reacts with the carbonic acid of the *bicarbonate*, thus releasing the insoluble *normal* carbonate. The soluble Na_2CO_3 , or $(\text{NH}_4)_2\text{CO}_3$, which is formed, precipitates the permanent hardness as CaCO_3 .

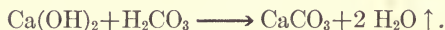


When the hardness is due to **magnesium** salts, sodium compounds, *not* ammonium compounds, are used to soften the water (*cf.* § 442).

The objection to hardness in a water used for generating steam is *partly* the fact that deposits of limestone, gypsum, etc., accumulate on the inside of the boiler ("boiler scale"), and cause waste of heat; but if the water contains calcium or magnesium *chlorides*, the hardness is much more serious, for these salts, especially the latter, are *hydrolyzed* at the high temperature of the boiler, producing *hydrochloric acid*, which "pits" the boiler (*cf.* § 442).

436. Calcium Phosphate, $\text{Ca}_3(\text{PO}_4)_2$. — Normal calcium phosphate occurs as *phosphorite*; combined with calcium chloride or fluoride it forms *apatite*, CaCl_2 (or CaF_2). $3 \text{Ca}_3(\text{PO}_4)_2$. Important deposits of these minerals ("rock phosphate") are found in Florida, South Carolina, Tennessee, etc. In 1910 the United States produced 2,655,000 long tons of rock phosphate. Most of it was used as fertilizer (*cf.* § 358). Calcium phosphate is the chief inorganic constituent of bones (*cf.* § 343).

437. Mortar, Cement, and Concrete. — When a thick paste of slaked lime and water is exposed to the air, it "sets," *i. e.*, becomes *dry* and *hard*. In the hardening, water escapes, and carbon dioxide unites with the slaked lime.



While "setting," mortar *contracts*. In mortars and cements this contraction is overcome by the use of *sand*. Sand also makes mortar *porous*, so that carbon dioxide can penetrate farther, and moisture can escape more easily. The sand should be *sharp*, so that it will become firmly imbedded in the crystals of calcium

carbonate as they are formed. Freshly plastered walls remain moist for some time, because the exchange of carbon dioxide for water is slow.

Cement. When limestone and clay (aluminum silicate; *cf.* § 393), or limestone containing naturally the right proportion of aluminum silicate, are heated together, there is formed a **cement**. This slakes slowly, and without much heat evolution, and has the valuable property of **hardening under water**. Hence it is called **hydraulic cement**.

Portland cement is made by heating to a high temperature an artificial mixture which contains the required proportions of *calcium oxide*, *aluminum oxide* (Al_2O_3), and *silica* (SiO_2), and then grinding the mass to a fine powder. Limestone, or marl, and shale, or clay, furnish the necessary constituents. Blast-furnace slag (*cf.* § 482) forms with limestone a similar mixture.

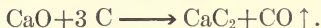
Cement probably consists of a mixture of *calcium silicate* ($\text{SiO}_2 \cdot 3 \text{CaO}$) and *calcium aluminate* ($\text{Al}_2\text{O}_3 \cdot 3 \text{CaO}$). Its hardening is, apparently, due to the union of its components with water of crystallization.

Concrete. Concrete is a mixture of water, cement, sand, and crushed stone. It hardens into a compact mass, and thus makes an excellent material for sidewalks, foundations and floors of buildings, and for structures under water, such as bridge-piers and the walls of dams. **Reënforced concrete** is concrete strengthened by rods of iron or steel, which are imbedded in it. It is used on an enormous scale for building purposes. In 1901 the United States produced about 20,000,000 barrels of cement; in 1910, almost 77,800,000 barrels.

438. Other Calcium Salts. — *Bleaching powder*, CaOCl_2 , has been described in §§ 122 and 329. If it were a *mixture* of $\text{Ca}(\text{OCl})_2 + \text{CaCl}_2$, alcohol would extract *calcium chloride* from it. Since this does not occur, it is assumed to be the **mixed salt**, CaOCl_2 .

Calcium silicate, CaSiO_3 , is a constituent of rocks and of glass (§ 394). It is made by mixing solutions of *sodium silicate* and *calcium chloride*, and by fusing **quartz** with **limestone**.

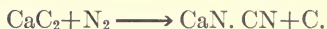
Calcium carbide, CaC_2 , is made by heating lime, or limestone, with coal, or coke, in the **electric furnace**.



The pure substance is a white, crystalline solid. The commercial product is dark, because impure. It reacts with water, giving **acetylene** (*cf.* § 295).

Calcium sulphide, CaS , is a white, soluble solid made by *reducing calcium sulphate* with carbon. It is a by-product in the Le Blanc soda process (*cf.* § 414). After the commercial sulphide has been exposed to sunlight, it **phosphoresces**; hence it is used in making **luminous paints** for match-boxes, clock-faces, etc. Barium and strontium sulphides have similar properties. The phosphorescence is due to *minute amounts of bismuth* compounds, etc. The pure sulphides do not phosphoresce.

Calcium Cyanamide, CaN_2CN , is formed by the reaction between **calcium carbide**, heated to white heat in an electric furnace, and **nitrogen**, which is conducted over it.

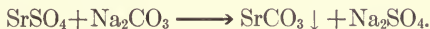


The product is used as a **fertilizer**. The water and oxygen of soil and air change it to *ammonia* and nitrates, both of which contain nitrogen in excellent form for plant food.

439. Strontium.

The compounds of strontium resemble those of calcium, but are less abundant and useful. **Strontium** is like calcium. It is made by the electrolysis of its chloride, SrCl_2 . With water it gives the *hydroxide*, Sr(OH)_2 , and hydrogen. The **oxide** is pre-

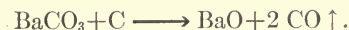
pared by heating the nitrate, $\text{Sr}(\text{NO}_3)_2$, (*cf.* § 230). The carbonate is decomposed by heat with great difficulty (see table, § 429). The oxide reacts with water and with carbon dioxide as lime does. The **sulphate** is "insoluble" (see table), but the **carbonate** is still *less soluble*; hence the former is converted into the latter when it is boiled with a soluble carbonate.



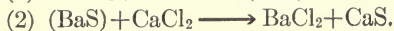
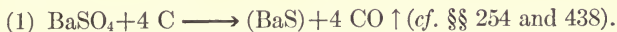
Strontium salts impart a red color to the non-luminous flame. The nitrate is used to prepare red lights and fireworks. The hydroxide is used in refining beet-sugar.

440. Barium.

Barium is like calcium and strontium. It is obtained by the electrolysis of its chloride, BaCl_2 . Barium occurs in nature as **witherite** (BaCO_3) and as **heavy spar**, or *barite*, BaSO_4 . Heavy spar has a specific gravity of 4.48. The **oxide** (BaO) is made by decomposing the nitrate, $\text{Ba}(\text{NO}_3)_2$, and by heating the carbonate with charcoal.



Note that this is, essentially, "removing the CO_2 from the 'sphere of action.' " The oxide unites with water, forming the **hydroxide**, $\text{Ba}(\text{OH})_2$. This crystallizes from water as $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$. Its solution is "baryta water" (*cf.* §§ 159 and 283). The **chloride** crystallizes as $\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$. It may be made from the oxide, sulphide, or carbonate and hydrochloric acid. It is also made by heating the sulphate with charcoal and calcium chloride.



Barium peroxide, BaO_2 , is formed when the oxide is heated to dull redness in the air. It is used to prepare oxygen (§ 22) and hydrogen peroxide (§ 339).

Barium salts impart a green color to the Bunsen flame. They should be moistened with concentrated c.p. hydrochloric acid before the flame test is applied. Barium nitrate and the chlorate $[\text{Ba}(\text{ClO}_3)_2]$ are used in making green lights and fireworks. Owing to the insolubility of barium sulphate, soluble barium salts are used to **test** for soluble sulphates, *i. e.*, ionic SO_4 .

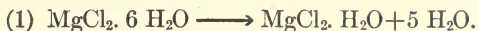
441. Magnesium. — Magnesium occurs in the Stassfurt deposits as *chloride* and *sulphate* (*cf.* § 420). It occurs also in **dolomite** ($\text{MgCO}_3 \cdot \text{CaCO}_3$), **magnesite** (MgCO_3), and in many **magnesium silicates**, such as *soapstone*, *meerschaum*, *serpentine*, and *asbestos*. The metal is prepared by the electrolysis of the mineral **carnallite**, $\text{MgCl}_2 \cdot \text{KCl} \cdot 6 \text{H}_2\text{O}$.

Magnesium is a silver-white metal with a high luster. It is light (see **table**), and oxidizes slowly in ordinary air. It burns in air with a flame of dazzling whiteness, giving the **oxide** (MgO) and the **nitride** (Mg_3N_2 ; *cf.* § 188). Magnesium does not react with water at the ordinary temperature (difference from the alkali and alkaline-earth metals, proper), but it burns vigorously when heated in *steam*. The light from burning magnesium is admirably adapted for photography; hence a mixture of the powdered metal and potassium chlorate is used for flash lights. Magnesium is also used for signal lights and in fireworks.

442. Magnesium Compounds. — *Magnesium oxide* (magnesia) is formed when the metal burns, and when the hydroxide and carbonate are heated. It

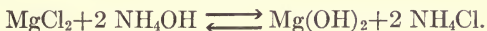
reacts *slowly* with water to give the insoluble **hydroxide**, $\text{Mg}(\text{OH})_2$. Magnesia is very *refractory*, i. e., hard to melt; hence it is used in making crucibles, cupels, fire-brick, and parts for electric furnaces.

Magnesium chloride forms deliquescent crystals ($\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$). When these are heated, the chloride is *hydrolyzed* (cf. § 435).



Magnesium sulphate, MgSO_4 , is called "Epsom salts." It is found in many springs, and in *kieserite* ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), etc. Kieserite unites with water to give $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$, which is the magnesium sulphate of commerce. Sodium sulphate is made from it (cf. § 419).

Magnesium hydroxide is precipitated from magnesium salts by sodium hydroxide; but only **incompletely** by *ammonium hydroxide*, owing to the reverse action.



If an excess of an ammonium salt is present, magnesium hydroxide is not precipitated at all by ammonium hydroxide, neither is magnesium carbonate precipitated, under the same conditions, by ammonium carbonate (cf. § 435). **Normal magnesium carbonate** is so readily hydrolyzed that the precipitate produced by alkali carbonates and magnesium salts always consists of the **basic carbonate**. Thus, "**magnesia alba**" is $\text{Mg}(\text{OH})_2 \cdot 3 \text{MgCO}_3$.

443. Radium.

The elements in the last **series** of the periodic table (§ 383) were, until 1898, *thorium* and *uranium*. The discovery of

radium came about in the following way:—Becquerel found, in 1896, that when uranium compounds (e. g., *pitchblende*, a uranium ore) are placed near photographic plates which are protected from light, they affect the plates like light itself. He ascribed the effect to *active rays* ("Becquerel rays") given off by the uranium. The simplest way to test for the presence of these rays, and for their amount, is to hold the material to be examined near a charged, insulated electroscope. If the material is "radio-active," the air becomes a conductor, and the electroscope is discharged. The time required measures the "radio-activity" of the substance. Professor and Mme. Curie, of Paris, removed the uranium compound from *pitchblende*, and found that the residue was still very active. By separating it carefully into its parts they obtained a small amount of *barium chloride*, and by analysis of this they secured a *minute* quantity of a new salt, **radium chloride**. This was more than 1,000,000 times as active as *pitchblende*. The properties of radium compounds place the element with the alkaline-earth metals, which are **bivalent**. The *equivalent weight* of the element was found, by analysis of the chloride, to be 113.2; hence the atomic weight is 226.4. In the periodic table it fills the space below barium. Radium compounds have the formulas RaCl_2 , Ra(OH)_2 , etc. All give off heat constantly, are self-luminous, and are strongly radio-active. In 1910 radium carbonate, RaCO_3 , was treated with *hydrazoic acid* (HN_3), and converted into the hydrazoate, $\text{Ra(N}_3)_2$. When this was heated in a vacuum, it broke up into *radium* and *nitrogen*. The radium had a metallic luster, and, like its salts, was radio-active.

The phenomena of radio-activity are explained by the assumption that the rays consist of particles, called **electrons**, or *corpuscles*, which are given off by the radio-active substance. Radium compounds also give off a gaseous material called **radium emanation**, or *niton*. This is condensed by liquid air. It belongs to the argon family, has the atomic weight 222.4,

and is in the same periodic *series* with radium, etc. When niton is examined with the spectroscope, it shows the spectrum of **helium**. Thus it appears that radium is constantly being formed by the "decay" of uranium, that niton is formed by the decay of radium, and that niton breaks down into helium, the element of lowest atomic weight in the argon family. The discovery that niton gives helium belongs to Sir William Ramsay, of London. He found, further, that when cupric nitrate is enclosed with niton, some **lithium nitrate** is formed. The copper is said to be "degraded" to lithium, the element of lowest atomic weight in the alkali family. Ramsay has also found that the elements of the carbon family, i. e., *thorium*, *zinc*, *titanium*, and *silicon*, are "degraded" by the "emanation" into **carbon**.

We must conclude, therefore, that some of the elements **decompose**, giving others of lower atomic weight. This does not do away with the conception of the atom, but, on the contrary, enlarges it.

444. Exercises.

1. How would you prove that some calcium nitride is formed when calcium burns in the air?

2. Magnesium liberates the hydrogen of ammonia; is ammonia, therefore, an acid?

3. Would you expect barium sulphate to be *soluble* in concentrated sulphuric acid (*cf.* § 267)? Name the product, and write the equation.

Does *carbonic acid* react with *barium carbonate*? Write the equation.

4. Write the equation for the preparation of the **oxide** of each of the alkaline-earth metals from its nitrate. Name these oxides in the order of their reactivity with water, beginning with the most active.

5. From the relative solubilities of barium carbonate and sulphate (*cf.* **Appendix viii**) would you expect to change the

latter into the former by boiling it with sodium carbonate solution? How could you separate a mixture of strontium and barium sulphates?

6. How could you separate the metal ions in a mixture of strontium chloride and magnesium chloride? Barium nitrate and potassium nitrate? Write the equations.

7. Write the partial and complete equations for the formation of *magnesia alba* from magnesium chloride.

CHAPTER XXXII.

ZINC, CADMIUM, AND MERCURY.

445. The Zinc Group. — The elements zinc, cadmium, and mercury are members of the *second group* of the periodic system. They are, however, much more closely related to magnesium than to the calcium group proper. Zinc and cadmium are very much alike, and are usually found together in nature; but mercury differs from them in some important respects. In the vapor state the molecules of all three contain one atom each (*cf.* § 142).

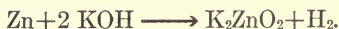
446. Zinc. — Zinc generally occurs in combination as the *sulphide*, ZnS , the *carbonate*, ZnCO_3 , and the *silicate*, Zn_2SiO_4 . The metallurgy of zinc is simple. Its ores are generally *roasted* to convert them into *oxide*, ZnO , and the oxide is reduced by charcoal.

The reduction of zinc oxide takes place in retorts or furnaces; from these the metal distills over into condensers. At first the vapors condense as a powder (*zinc dust*); afterwards the metal condenses as a liquid, and is cast into plates and bars. The zinc thus obtained (called *spelter*) is not pure. Pure zinc is obtained by the electrolysis of zinc chloride.

447. Properties. — Zinc is a white, hard, and lustrous metal. In dry air it does not change; but

ordinarily its luster is soon dulled by a covering of basic carbonate. At the ordinary temperature, zinc is *brittle*; but between 100° C. and 150° C. it can be rolled into sheets and drawn into wire. At higher temperatures it is so brittle that it can be powdered.

Zinc melts at 420° C., and boils at 920° C. When heated much above the melting-point, it burns to zinc oxide. Water does not affect the metal, even at 100° C. Hot solutions of alkali hydroxides react with it, forming *zincates* and hydrogen (*cf.* §§ 57, 388, and 474).



Commercial zinc reacts readily with all the ordinary acids; but the pure metal requires a catalyzer, such as copper or platinum (*cf.* § 47.)

448. Uses. — Zinc is used for the positive plates of electric batteries and in **alloys**, e. g., *brass* (*cf.* § 458), *German silver*, etc.

Galvanized iron is iron coated with zinc by dipping it into a bath of molten zinc. Galvanized iron resists the action of air and moisture better than *tinned* iron. It is used for wire netting, corrugated roofing, gutters, water-tanks, etc.

449. Zinc Compounds. — Among the important zinc compounds are the *oxide*, *hydroxide*, *chloride*, *sulphate*, and *sulphide*. Soluble zinc salts are poisonous.

Zinc oxide, ZnO , can be made by burning zinc, and by heating the carbonate or nitrate (*cf.* § 230). When hot it is *yellow*; when cold, *white*. It is sold as the pigment, **zinc white**.

Zinc hydroxide, Zn(OH)_2 , is precipitated when zinc salts react with soluble hydroxides. It *redissolves in an excess* of alkali hydroxides, giving **zincates**.

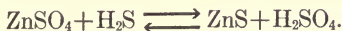
Zinc chloride, ZnCl_2 , may be formed by treating the metal with hydrochloric acid (*cf.* § 47). It is a white, deliquescent solid that fuses readily and distills without decomposing. It is usually cast in sticks.

Zinc sulphate, ZnSO_4 , is formed from the metal and *dilute* sulphuric acid. Large quantities are made by roasting the natural *sulphide*, ZnS , and extracting with water.



From water the sulphate separates as transparent crystals of "**white vitriol**," $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$.

Zinc sulphide, ZnS , separates as a *white* precipitate when an alkaline sulphide is added to the solution of a zinc salt. Zinc sulphide belongs to the "moderately insoluble" sulphides (*cf.* § 255). It is precipitated only partly by hydrogen sulphide, because of the *reverse action*. If acid is present, it is not precipitated at all.



450. Cadmium.—Cadmium is similar to zinc, melts at 320°C ., boils at 749°C ., and is used in making some *alloys* (*cf.* § 374). The *sulphide*, CdS , forms a beautiful, yellow pigment, which is **not** soluble in alkali sulphides (*cf.* §§ 365, 369, and 516).

451. Mercury.—Mercury, or *quicksilver*, occurs native in some of its ores; but the principal source of it is *cinnabar*, HgS . Cinnabar is mined chiefly in

Spain and California; recently deposits have been found in Texas. Mercury is obtained from its ore by *roasting*. The sulphur passes off as sulphur dioxide; while the mercury vapors are condensed.

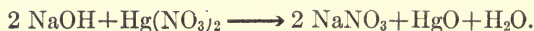
452. Properties and Uses. — Mercury is a white, lustrous liquid. It is 13.6 times as heavy as water, solidifies at -39.5°C. , and boils at 357°C.

Mercury does not react with hydrochloric acid nor with *cold* sulphuric acid. Hot, concentrated sulphuric acid attacks it (*cf.* § 265); so does *nitric acid*. If the nitric acid is *dilute* and *cold*, and the mercury is in *excess*, the salt formed is *mercurous nitrate*, HgNO_3 ; if the *concentrated* acid is used, and the mercury is completely used up, *mercuric nitrate*, $\text{Hg}(\text{NO}_3)_2$, is formed. Both nitrates are white, crystalline solids. Mercury vapor and soluble mercury salts are very poisonous.

Mercury is used in extracting gold and silver from their ores, in amalgamating battery zincs, and in making thermometers, barometers, air-pumps, percussion caps, etc.

453. Mercury Compounds.

Mercuric oxide, HgO , also known as “red precipitate,” may be made by long heating of the metal almost to its boiling temperature in contact with air. It is *usually* prepared by heating the *nitrate* $\text{Hg}(\text{NO}_3)_2$ (*cf.* § 449; *zinc oxide*). Another form is **yellow** in color; this is prepared by adding an alkali to the solution of a mercuric salt.



The **hydroxides** of mercury lose water spontaneously, giving the *oxides*. The effect of heat upon the oxide is described in § 16.

Mercurous oxide, Hg_2O , is formed when an alkali is added to a *mercurous salt*.

Mercurous chloride, HgCl , is known as *calomel*, and is an important medicine. It is precipitated when a solution of a chloride is added to a solution of a mercurous salt.

It is commonly made by subliming a mixture of mercury and *mercuric chloride*,



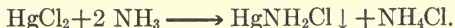
The **reverse** action takes place in the light; hence calomel must be kept in the dark, or it will contain *corrosive sublimate*.

Mercuric chloride, HgCl_2 , is commonly called *corrosive sublimate*. It is made by subliming a mixture of *mercuric sulphate* and *sodium chloride*.

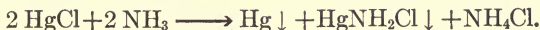


Mercuric chloride is a white, crystalline solid; it is easily soluble in water, and very poisonous. It is used extensively in surgery (usually one part in 1,000 parts of water) because of its powerful antiseptic action. For its *reduction* by stannous chloride cf. §§ 181 and 516.

Mercuric chloride and nitrate react with ammonium hydroxide, giving white precipitates of HgNH_2Cl and HgNH_2NO_3 , respectively. They are "**mercur-ammonium**" salts.



Mercurous chloride and nitrate give corresponding salts, but they are **black**, because mixed with finely divided mercury.



Mercuric sulphide, HgS , occurs as *cinnabar* (§ 451), a red, crystalline solid. The sulphide may be made by rubbing together *mercury* and *sulphur*, and by passing *hydrogen sulphide*

into the solution of a mercuric salt. In both cases the mercuric sulphide will be black; but when it is sublimed it yields *red* crystals. The red product is the pigment, "Chinese vermilion." Mercuric sulphide is not affected by dilute acids. **Mercurous sulphide** is precipitated from mercurous salts by hydrogen sulphide, but decomposes spontaneously, giving mercuric sulphide and mercury.

Mercuric iodide, HgI_2 , is precipitated when a potassium iodide solution is added to one of a mercuric salt. An excess of potassium iodide redissolves the precipitate, owing to the formation of K_2HgI_4 , which is *soluble*. Mercuric iodide is also made by triturating a mixture of potassium iodide and mercuric chloride, or of mercury with an excess of iodine, in a mortar. It is a bright-red powder, soluble in hot alcohol and in ether. When heated, the dry powder gives a **yellow** sublimate; this reverts to the red form, when rubbed, **with evolution of heat** (cf. § 249). Mercuric iodide is used as an **antiseptic**, replacing the chloride.

Mercurous iodide, HgI , is a yellow-green powder obtained from a *mercurous* salt solution and potassium iodide, also by grinding iodine with the calculated amount of mercury. It is insoluble in alcohol and in ether, and is changed by the light, and by potassium iodide solution, into the mercuric salt and mercury.

Mercuric fulminate, $\text{Hg}(\text{ONC})_2$, is used for percussion caps.

Sodium amalgam was described in §§ 403 and 411. **Tin amalgam** was formerly used in making mirrors. **Zinc amalgam** is formed on the positive plate when battery zincs are "amalgamated." Several amalgams have been used for soft fillings by dentists.

454. Exercises.

1. Write equations, partial and complete, for the following reactions: —

- (a) Zinc sulphate solution with excess of sodium hydroxide.
 - (b) Preparation of mercury from cinnabar, and of mercurous and mercuric nitrates from mercury.
 - (c) Preparation of mercuric oxide from the nitrate, by heat.
 - (d) Preparation of cadmium oxide, sulphate, chloride, and sulphide.
 - (e) Mercurous nitrate solution and hydrogen sulphide.
 - (f) Mercuric sulphate solution with potassium iodide (excess).
 - (g) Action of mercurous iodide with potassium iodide.
 - (h) Action of sodium amalgam with water.
2. Give all the changes that would take place if sodium zincate solution were treated with hydrochloric acid, drop by drop, until there was an excess.
3. Give characteristic tests for mercury, zinc, and cadmium, by which you can distinguish between them.
4. How could you separate a mixture of *mercurous*, *mercuric* and *zinc* ions, so as to get each in the form of a precipitate? Write the equations.

CHAPTER XXXIII.

COPPER, SILVER, AND GOLD.

455. Relation of Copper, etc., to the Alkali Metals.

— Copper, silver, and gold are in most respects different from the other members of the first periodic group, but are related to these elements — the alkali metals — much as zinc, cadmium, and mercury are related to the calcium group.

They are not changed by *water* or by *pure* air; hence they occur *native* as well as combined with other elements. Because they occur native all three have been known for thousands of years, while none of the alkali metals was known until 1807.

456. Occurrence and Metallurgy of Copper. —

Copper is abundant and widely distributed. It occurs *native*, especially in the Lake Superior region, and in combination as *ruby copper*, Cu_2O ; *malachite*, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$; *chalcocite*, Cu_2S ; and *copper pyrites*, $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$. *Bornite* is $(\text{Cu}_2\text{S})_3 \cdot \text{Fe}_2\text{S}_3$; *azurite*, $\text{Cu}(\text{OH})_2 \cdot 2 \text{CuCO}_3$.

Of the world's supply of copper, the United States produces more than half: 504,000 tons in 1910.

Native copper is obtained by crushing the ore, washing away the lighter particles, and smelting and refining the concentrated "mineral." Lake Superior ore has from 0.75% to 5% of copper.

Oxide, hydroxide, and carbonate ores are smelted with coke in blast-furnaces. One fusion often yields a 96% copper.

Sulphide ores usually contain iron, as well as lead, arsenic, etc. Except for ores of very low grade, the processes are as follows:—

1. The ores are *concentrated* by crushing and washing, and are then **roasted** (cf. § 252), to remove most of the sulphur. The *sulphur dioxide* produced may be used for sulphuric acid. Part of the *iron* becomes **iron oxide**, and most of the *copper*, **copper oxide**.

2. The roasted ore is then mixed with *coke*, to reduce the copper oxide, and with *acid silicates*, to unite with the iron oxide. The mixture is smelted in a blast-furnace (cf. § 482; Fig. 88). *Iron silicate* is formed as a light slag that can be drawn off, while the heavy liquid below it consists largely of the sulphides of iron and copper. It contains from 30% to 60% copper, and is called "**matte**."

3. The **third** operation is the formation of "**blister copper**," by the oxidation of the matte in a **Bessemer "converter,"** like the one used in making steel (cf. § 487; Fig. 90). In the "converter" a blast of hot air, sometimes containing sand, is forced up through the melted matte, and removes most of the remaining sulphur, arsenic, antimony, lead, and iron, as *oxides*. The volatile oxides escape, while the non-volatile ones form a scum on the surface, or unite with the silica, with which the converter is lined, to form silicates, or **slags**. Some of the copper oxide formed reacts with cuprous sulphide:



Occluded sulphur dioxide (cf. §§ 53 and 463), which escapes when the copper solidifies, gives the metal a characteristic blistered appearance.

4. The air-blast of the converter oxidizes some of the copper. The process called "**poling**" consists in reducing the copper

oxide by stirring the melted blister copper in a *reverberatory furnace* (cf. § 462; Fig. 86) with long poles of "green" wood. Finally, the product is cast in the form of thick plates called "anodes," and *refined* by electrolysis.

5. Refining of Copper. The refining process (Fig. 85) consists in making the thick plates of impure copper the **anodes** of electrolytic cells containing cupric sulphate solution; while a thin plate of pure copper forms the cathode. The anode wastes away, and its copper is deposited, in pure form, upon the cathode. Many copper ores contain small amounts of gold and silver,

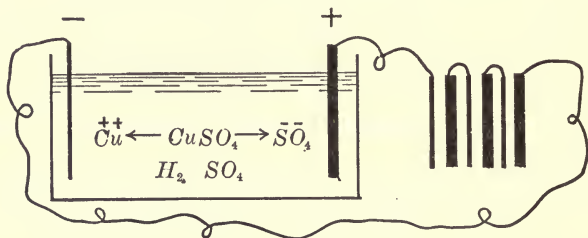


FIG. 85.

and these accompany the copper *up to* the refining process. In the electrolysis, however, the precious metals, along with some cuprous sulphide, lead, and bismuth, are left in the refining tanks as "mud." This is collected, and the gold and silver are extracted from it.

457. Properties. — Copper has a red color, and is ductile and malleable. It melts at about 1080°C ., while silver melts at 954°C . and gold at 1060°C . Copper is the best conductor of electricity known, except *silver*; *iron* is the only metal having greater tensile strength. The specific gravity of copper is 8.9.

In the atmosphere copper becomes coated with the basic carbonate (cf. *malachite*, § 456). The action of nitric acid and sulphuric acid upon copper has been discussed in §§ 227 and 265, respectively. Hot, concentrated hydrochloric acid reacts slightly with it, giving **cuprous** chloride and hydrogen. Dilute acids act on it slowly, *in the presence of air*, giving cupric salts. The sulphate is made in this way.



Copper may be separated from solutions of its salts by *zinc*, *iron*, etc., and by *electrolysis*.

458. Uses. — Copper is used as an electric conductor, as ships' *sheathing* and *bolts*, and for electrical apparatus, utensils, coins, boilers, stills, etc. It is used, also, in *copper-plating* and *electrotyping*, and as a part of many *alloys*.

Brass usually contains 28% to 34% *zinc* and the remainder copper.

Bronze contains copper, zinc, and tin.

Gun-metal is about 90% copper and 10% tin.

Bell-metal consists of *copper*, about 75%, and *tin*, 25%.

German silver is, *approximately*, 50% *copper*, 30% *zinc*, and 20% *nickel*.

Aluminum bronze is copper with 5% to 10% of aluminum. It has the color of gold, is hard and elastic, and does not tarnish easily. Aluminum containing 3% of copper is *whiter* than pure aluminum.

459. Copper Compounds. — Copper, like mercury, iron, etc., forms *two* series of compounds: *cuprous* and *cupric* compounds (cf. §§ 111 and 169). Examples are:

Cuprous chloride, CuCl or Cu_2Cl_2 .

Cupric chloride, CuCl_2 .

Cuprous oxide, Cu_2O .

Cupric oxide, CuO .

Cuprous sulphide, Cu_2S .

Cupric sulphide, CuS .

In the *cupric* compounds copper is evidently *bivalent*. If copper is bivalent in the *cuprous* compounds of the halogens, e. g., in *cuprous chloride*, the simpler formula must be doubled.

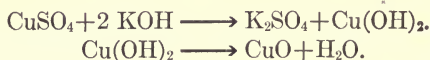
The constitutional formula will then be

$$\begin{array}{c} \text{Cu} - \text{Cl} \\ | \\ \text{Cu} - \text{Cl} \end{array}$$

Cuprous oxide occurs naturally as “ruby copper.” It is formed as a black scale when the metal is heated in the air, and as a red precipitate when a solution of a cupric salt is heated with the solution of an alkali in the presence of a suitable reducing agent, e. g., *grape-sugar*, $\text{C}_6\text{H}_{12}\text{O}_6$.

Cuprous sulphide is made by heating copper with sulphur.

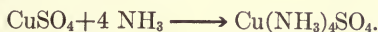
Cupric oxide is formed by treating a boiling solution of a cupric salt with the solution of an alkali. The blue cupric *hydroxide*, $\text{Cu}(\text{OH})_2$, which is formed if the solution is cold, cannot exist in the boiling solution.



Cupric sulphate pentahydrate is blue vitriol (*cf.* § 88). The anhydrous salt is **white**. It dissolves in hot, concentrated sulphuric acid, and separates, when cold, in white crystals. Blue vitriol is used in making blue and green pigments, in copper-plating, in preserving wood, and for gravity batteries. It is also used extensively in agriculture as a *germicide* and *fungicide*. The **Bordeaux mixture** consists of calcium hydroxide and cupric sulphate. A minute amount of cupric sulphate, too small to kill larger water animals, is able to destroy the algæ of ponds and water reservoirs, and so to purify the water.

Cupric sulphide, CuS , is a heavy, black solid, precipitated when cupric salts in solution are treated with hydrogen sulphide or with alkaline sulphides.

Cupric salts react with excess of ammonia-water to give solutions of deep-blue color.



The deep-blue color is due to the complex, bivalent, positive ions, $\text{Cu}(\text{NH}_3)_4^{++}$.

460. Copper-plating. — An object that is to be plated with copper is put into a bath of some copper salt in solution, and connected with the kathode of a battery or dynamo circuit (*cf.* Fig. 85). A bar of copper is used for the anode. The bar of copper is gradually used up, and copper is deposited upon the object to be plated. The bath does not deteriorate.

This process is used in making *electrotype plates*, either from type or from woodcuts. An impression of the type or wood cut is first made in plaster of Paris; this is covered with graphite powder and placed in the copper-plating bath as the *kathode*. The plate produced is an exact reproduction of the type or wood-cut from which the plaster impression was taken.

461. Silver. — Silver is found native; also combined with sulphur and with the sulphides of other metals. The lead ore, *galena* (PbS), usually contains silver. The natural chloride, AgCl , is called “horn silver.”

Most of the world's silver is found in the United States, Mexico, Bolivia, and Australia. The United

States produced, in 1910, 57,137,900 ounces — about one third of the world's supply for that year.

462. Extraction of Silver from its Ores. — Silver is separated from its ores by various processes; we shall consider only *two*, viz., the *Amalgamation Process* and the *Smelting Process*.

The **Amalgamation Process** consists in extracting the metal with mercury, after a preparatory treatment. This treatment consists in *crushing* the ore, *roasting* it with salt to change the

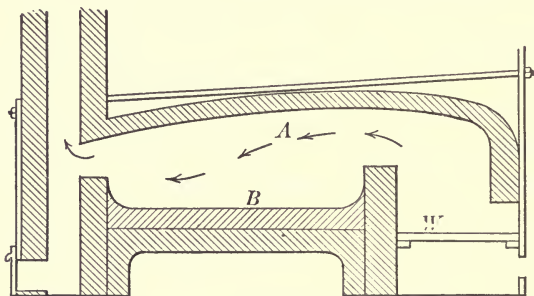


FIG. 86.

REVERBERATORY FURNACE.

(The fuel burns at *W*; the substance to be heated is placed on the hearth *B*. The curved roof *A* directs the hot gases of *W* down upon *B*.)

sulphide into the *chloride* of silver, and then reducing the chloride to silver by means of water and iron. The mass is then mixed with mercury, and the resulting *amalgam* is collected, dried, and heated in retorts. The mercury distills off, and is ready to be used again; the silver is then separated from whatever **gold** is present, as described at the end of this section.

Smelting Process. — Silver ores usually contain lead, and lead ores often have enough silver to pay for its removal; hence

the reduction of the two metals is carried out in a single smelting operation.

The lead ore is *roasted* to remove sulphur, and then *reduced* with coke in a blast-furnace. The silver and the gold present remain alloyed with the lead. The resulting crude lead (known as **base bullion**) is then heated in a **reverberatory furnace** (Fig. 86), and stirred frequently. The small quantities of copper, arsenic, and antimony present are thus oxidized, and are skimmed from the surface as *dross*. What remains is a mixture of *lead, silver, and gold*. Most of the lead is now removed by the **Parkes Process**. This consists in melting the metal in large iron pots, adding 1% to 2% of **zinc** and stirring. When the mixture is cooled slowly, an alloy of zinc, silver, and gold, with but little lead, comes to the surface, solidifies, and is skimmed off. If necessary, zinc is added a second or even a third time. The skimmings are then heated in **graphite** retorts (*cf.* § 272); and the zinc is distilled off, condensed, and cast into slabs to be used again. The residue in the retort consists of lead, silver, and gold. The lead is now completely removed from the precious metals by oxidizing it with hot air in a shallow furnace. The lead oxide (*litharge*, PbO) flows off from the top of the furnace.

Gold is separated from silver by treating the mixture of these metals with nitric acid, or hot, concentrated sulphuric acid. The gold is not acted upon.

The sulphuric acid separation is carried out in iron kettles. The silver sulphate formed is treated, in solution, with copper, which precipitates *silver*. This is melted and cast into *ingots*.

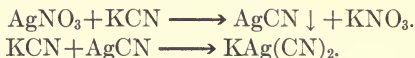
463. Properties. — Silver is a white metal, capable of receiving a mirror-like polish. It conducts heat and electricity better than any other metal, and is malleable and ductile. It melts at 954°C. , and boils

in the oxyhydrogen flame. Melted silver absorbs about twenty-two times its own volume of oxygen; when the silver solidifies, the gas is given off ("spitting" of silver).

Silver does not tarnish in pure air, but is quickly blackened by sulphur compounds (*cf.* § 250). Hydrochloric acid does not attack it. Nitric acid and hot, concentrated sulphuric acid act upon it as upon copper.

464. Uses. — Silver is used for *coinage*, tableware, jewelry, ornaments, and mirrors, and for *plating* other metals. Pure silver is very soft, and is therefore alloyed with copper. The silver coins of the United States and of France contain 90% silver ("coin silver"), and are said to be 900 *fine*. The grade 925 *fine* is called "sterling silver"; British silver coins are of this grade.

Silver-plating is usually done by electrolysis of the *double cyanide of silver and potassium*. A bar of silver forms the anode, and the object to be plated, the kathode (*cf.* § 460). The rough or "matt" surface is given the usual lustrous finish by polishing with chalk. The double cyanide solution is made by adding to a silver nitrate solution one of *potassium cyanide* (*cf.* § 426) until the silver cyanide first precipitated is redissolved.



The silver forms part of the complex **negative** ions, $\text{Ag}(\text{CN})_2^-$.

Mirrors are made by precipitating silver upon glass. The silver is deposited from silver nitrate solution containing am-

monia. This solution and a suitable reducing agent, *e. g.*, ammonium tartrate, or acetaldehyde (CH_3CHO), are put upon the glass, and the glass is gently heated. The bright deposit of silver is washed, dried, and covered with varnish to protect it from the hydrogen sulphide, etc., of the air.

465. Compounds of Silver. — *Silver nitrate*, AgNO_3 , is the most important compound of silver. It is a white, crystalline solid, made by treating silver with dilute nitric acid. Silver nitrate is sometimes called *lunar caustic*. Silver sulphate, Ag_2SO_4 , is also soluble.

Silver chloride, AgCl , *silver bromide*, AgBr , and *silver iodide*, AgI (*cf.* § 335), are made by adding solutions of chlorides, bromides, and iodides, respectively, to solutions of silver salts. They are affected by light, and are used in photography.

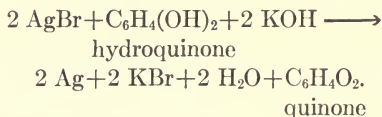
Silver chloride and bromide “dissolve” in ammonia-water, giving soluble salts, $\text{Ag}(\text{NH}_3)_2\text{Cl}$ and $\text{Ag}(\text{NH}_3)_2\text{Br}$. In these the silver is part of the complex **positive** ion, $\text{Ag}(\text{NH}_3)_2^+$. Soluble silver salts, such as the nitrate, give a precipitate with a *little* ammonium hydroxide, but it redissolves in an excess, owing to the formation of soluble compounds containing the complex ion.

466. Photography.

Silver salts are used in photography because they change color and become insoluble in certain chemicals after being exposed to light. When a photographic plate is exposed in a camera, no change is visible until the plate has been **developed**. Developing consists in treating the plate with a *reducing* agent, such as

ferrous sulphate, pyrogalllic acid, hydroquinone, eikonogen, etc. When the plate is covered with the developing solution, an image appears; this is due to the precipitation of a film of *silver*, which produces variations of light and shade. Where the light acted *strongly* upon the plate, the deposit of silver is relatively heavy; and where there was little action, there is little metal deposited.

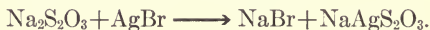
Just what the action of light upon the silver bromide of a plate is, is not definitely known, but it certainly makes the reduction to silver take place more easily than is the case with *ordinary* silver bromide. The action of a developer may be illustrated by the following equation: —



In this case the *reduction* of the silver bromide is due to the *oxidation* of *hydroquinone* to *quinone*.

Fixing.—When the plate is sufficiently *developed*, it is rinsed and put into a bath of *sodium thiosulphate* (“*hypo*”; cf. § 268) to remove the silver salts not acted upon by light. This **fixes** the negative. The plate is called a “*negative*” because in it dark objects appear light, and light objects dark.

The action of sodium thiosulphate upon silver salts is to form the *soluble* “*mixed*” salt, NaAgS_2O_3 .



A “**print**” is made by placing the film of a sensitized paper next to the negative and exposing both so that the light passes through the negative. The image may appear on the paper *at once* (“*printing-out*” papers) or may have to be *developed* (“*developing*” papers). In either case the prints are “*fixed*” by removing the unchanged silver salt.

Toning.—Some papers are “**toned**” in a bath of *gold chloride*,

AuCl_3 , or *platinum chloride*, PtCl_4 , before fixing. Toning replaces part of the silver by gold or platinum.

Blue prints are made on paper coated with a *ferric salt* (ferric ammonium citrate) and *potassium ferricyanide*, $\text{K}_3\text{Fe}(\text{CN})_6$. After exposure, the picture is developed and fixed by washing it in water. The result is a blue print on a white ground. The process is used for copying *plans*, etc.

467. Gold. — Gold is found both native and combined. Even *native* gold is not pure, however, but contains silver, and often iron, copper, etc. The metal is frequently found enclosed in *quartz* or *quartz-sand*.

Gold is obtained chiefly from Colorado and other western states, from Alaska, and from Australia, Siberia, and South Africa. The gold produced in the United States during 1910 was 4,657,018 fine ounces, worth \$96,269,100. This was about *one-fourth* of the world's yield that year.

468. Metallurgy of Gold. — Gold-mining is of *two* general kinds: (1) *placer-mining*, and (2) *vein-mining*.

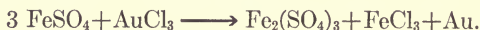
In **placer-mining** the clay and sand containing the gold are washed with water. The lighter particles are thus removed; while the gold and other heavy metals remain. Gold and silver are extracted from this mixture by mercury (cf. § 462; *amalgamation*).

Vein-mining consists in removing the gold-bearing rock from the earth and crushing it in stamp mills. The lighter materials are then washed away, and the gold is collected with mercury, as in placer-mining. **Hydraulic-mining** is a form of placer-mining done on a large scale with powerful streams of water.

Instead of mercury, **chlorine** and **bromine** are used to remove gold from the crushed ore. They form the soluble *gold chloride*, AuCl_3 , or *bromide*, AuBr_3 . This is extracted with water, and the gold is precipitated by means of *charcoal* or *ferrous sulphate* (cf. § 469).

The **Cyanide Process** depends upon the fact that gold is converted into the soluble double cyanide, $\text{KCN} \cdot \text{AuCN}$, by a solution of the alkali cyanides. The gold is separated from the cyanide solution by electrolysis or by means of zinc.

469. Purification of Gold. — The gold obtained by the processes described above is not pure. It can be separated from silver by adding *aqua regia*, which reacts with the gold. The solution is evaporated to remove nitric acid, the residue is dissolved in water, and the gold is precipitated by *ferrous sulphate* or some other *reducing* agent.



In the treatment of silver and gold with sulphuric acid (cf. § 462, *end*) gold is left in the kettle as a brown, spongy mass. This is washed, dried, and melted in a crucible with charcoal and sodium carbonate. The resulting product, *chemically pure* gold, is poured into a mold, and leaves it as a *gold brick*.

470. Properties and Uses. — Gold is the only *common* metal that is yellow. It is a good conductor, and the most ductile and malleable substance known. Its specific gravity is 19.3, and its melting temperature 1060°C .

Gold unites directly with *chlorine* and *bromine*, but not with oxygen. *Aqua regia* reacts with gold, form-

ing *auric chloride*, AuCl_3 (cf. § 466; "toning"); but the common acids do not affect it.

Gold is the *standard* of coinage of most nations. It is hardened by alloying it with copper (10% in the United States). For jewelry the proportion of gold varies from 40% to 75%; it is usually given as so many "*carats fine*." Pure gold is 24 carats fine; hence 18-carat gold is 75% gold and 25% alloy. Because of its *malleability* and weak chemical action, gold is much used by dentists for filling teeth. Gold-leaf is used in ornamentation.

471. Exercises.

1. What are the atomic weights of copper, silver, and gold, respectively? Which forms the most *stable* oxide (cf. § 405)? The least? Which is affected most readily by the air?

2. In the heating of copper *matte* in a "converter," why are arsenic, lead, and iron oxidized before copper? Which of these form *volatile* oxides? What materials might "green" wood yield in the "poling" process that could reduce copper oxide?

3. Cupric oxide "dissolves" in warm, concentrated hydrochloric acid. Write the equation. When the solution is heated with copper, a white solid separates out. What is it? Write the equation for its formation.

4. From the difference in the solubilities of silver chloride, bromide, and iodide (cf. **Appendix viii**), what would happen if the chloride and bromide were heated with a solution of potassium iodide? Give the equations.

5. How would you distinguish between the nitrates of barium, copper, cadmium, zinc, mercury (ic), and silver?

6. How would you separate the copper and silver of a silver coin so as to recover each metal in the free state? Write all the equations.

7. How would you separate brass into copper and zinc?

8. Give the uses of the **alloys** named in this chapter.

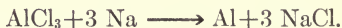
CHAPTER XXXIV.

ALUMINUM.

472. Occurrence of Aluminum. — Although aluminum does not occur *free*, it is the most abundant and widely distributed metal. Only oxygen and silicon are more abundant. Some of its most important minerals are *potash feldspar* (KAlSi_3O_8), *mica* (*muscovite*), $\text{H}_2\text{KAl}_3(\text{SiO}_4)_3$, and *cryolite* (*cf.* § 316). *Granite* is a mixture of *quartz*, *feldspar*, and *mica*. *Clay* results when granite and similar minerals are decomposed (*cf.* § 10).

All the other elements of the aluminum group are rare (*cf.* Periodic Table, § 383).

473. Preparation. — Aluminum was formerly produced from *anhydrous* aluminum chloride and sodium.



This method has been superseded by electrolytic processes, of which that of Hall (1887) is perhaps the most important. This is carried out on a large scale at Niagara.

Hall's Process. — The furnace used in the Hall process is a box of boiler iron (Fig. 87), the bottom and sides of which are lined with a mixture of coke and tar, rammed hard. The bot-

tom forms the $-$ electrode, while the $+$ electrode consists of forty large carbons suspended by copper rods.

To begin the process, the carbons are lowered *almost* to the bottom of the furnace, *cryolite* is put in, and the current is turned on. The resistance to the passage of the current produces heat enough to melt the cryolite. Pure, dry *aluminum oxide*, Al_2O_3 , is then mixed with the fused cryolite, and the electrolysis begins.

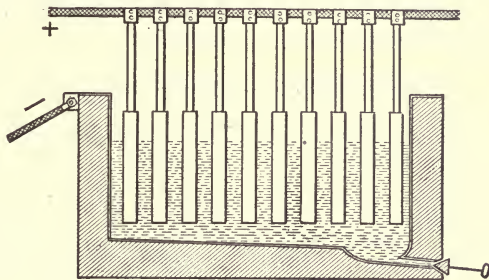


FIG. 87.

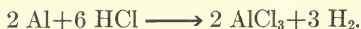
The process is **continuous**, for the cryolite bath remains unchanged. The aluminum collects at the bottom, and is drawn off; the *oxygen* of the aluminum oxide unites with the carbons to form *carbon monoxide*, which escapes. The United States consumed over 21,600 metric tons of aluminum in 1910; this was probably over two-thirds of the world's output.

The aluminum oxide used is obtained from *beauxite* (or *bauxite*), $\text{Al}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$. The natural mineral has impurities, *e. g.*, *iron*, *silicon*, etc.; these are removed at present by fusing the *beauxite* with a little metallic aluminum.

474. Properties.—Aluminum is a white, lustrous metal. Its specific gravity (2.6) is very low compared with that of other common metals, zinc being 7.1 and

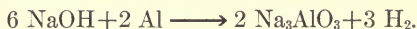
iron 7.8 times as heavy as water. It melts at about 660°C . and vaporizes at the temperature of the electric furnace. Aluminum is a good conductor, is ductile and malleable, and has the tensile strength of cast-iron. *Commercial* aluminum is 95% to 99.6% pure.

At white heat aluminum burns to *aluminum oxide*, Al_2O_3 . Hydrochloric acid readily reacts with the metal, forming *aluminum chloride*.



Nitric acid and dilute sulphuric acid do not act upon it ordinarily.

Aluminum reacts with solutions of salt and other chlorides if a little free acid is present. It reacts, also, with the hydroxides of sodium and potassium, forming *aluminates* and *hydrogen*.



Aluminum unites directly with the *halogens*, and with *carbon*, *silicon*, *nitrogen*, etc.

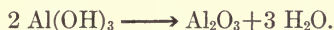
475. Uses. — It is probable that more aluminum is used in the manufacture of iron and steel than for any other *one* purpose. The aluminum removes any oxygen the iron may have in combination, and thus increases the fluidity of cast-iron and steel.

The next important use is as a conductor of electricity. The Northwestern Elevated Railroad of Chicago is using twenty miles of $1\frac{1}{2}$ -inch aluminum

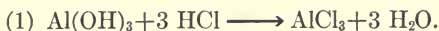
cables, weighing 150,000 pounds, to transmit motive power to its trolley cars.

Aluminum *powder* is used to reduce the oxides of many metals, e. g., *chromic oxide*, Cr_2O_3 , in *thermite* (cf. § 308), and for flash-lights. A large part of the aluminum produced is used for kitchen utensils, scientific instruments, etc.; the aluminum **alloys** also require much of the metal. The alloys with copper were described in § 458. The alloy **magnalium** contains 75% to 90% aluminum and the remainder *magnesium*. It is light, hard, and takes a high polish.

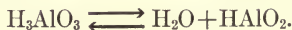
476. Aluminum Oxide and Hydroxide. — Aluminum oxide, Al_2O_3 , occurs in the form of *ruby*, *sapphire*, and *corundum*. *Emery*, an impure form of corundum, is very hard, and is used for grinding and polishing. *Alundum* is an artificial corundum made by melting bauxite in the electric furnace. Aluminum oxide may be made by heating the *hydroxide*.



Aluminum hydroxide, $\text{Al}(\text{OH})_3$, may be precipitated by adding *ammonium hydroxide* to the solution of an aluminum salt, e. g., *aluminum chloride*. Aluminum hydroxide reacts with both acids and alkalies (except ammonium hydroxide); with acids it gives *aluminum salts*, and with alkalies, *aluminates* (cf. § 474). It is, therefore, a *base* toward strong acids and an *acid* toward strong bases (cf. §§ 363 and 368).

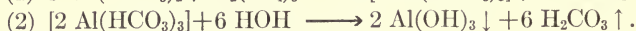


Many aluminates are derived from the **meta** form, HAlO_2 .



477. Uses of Aluminum Hydroxide.

As stated in § 69 (*q.v.*), aluminum hydroxide has the power of entangling finely suspended clay and the germs clinging to it, and is, therefore, used **to purify water by coagulation**. The “*temporary hardness*” of the water (*cf.* §§ 284 and 435) may be sufficiently abundant to produce the precipitate (*cf.* § 478); if not, lime is used.



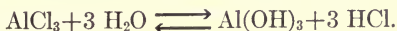
Mordants.— Just as precipitated aluminum hydroxide takes up suspended clay particles, so it removes many coloring matters from solution. The aluminum hydroxide and coloring matter form a **lake**. The aluminum hydroxide acts in the same way when it is deposited in the fibers of cloth, and thus serves to “*fix*” dyes in fabrics that do not readily hold color. When so used, the hydroxide is called a **mordant**, from the Latin “*to bite*”: the mordant “*bites into*” the fabric. The aluminum hydroxide is precipitated in the cloth fibers by soaking the cloth in aluminum salts, such as the *acetate*, and then hydrolyzing the salts with steam, or by soaking the cloth, first, in the salts, and then in ammonia water. Salts of tin, chromium, iron, and copper may be used instead of aluminum salts, for all give gelatinous precipitates either when hydrolyzed, or when treated with ammonia. *Tannic acid* is also used. In making calico, the pattern is printed with a mordant, and the cloth is then exposed to a dye which combines with the mordant, but not with the cloth. The uncombined dye is washed out. Different parts of the pattern may be printed with different mordants; thus a number of colors may result from the same dye.

Dyes. The union of fabric with dye-stuff, either with or without a mordant, is partly chemical and partly physical. The different characters of the fibers of cotton, linen, wool, and silk bring about physical differences in their dyeing. The chemical differences are more important; for cotton and linen are chiefly *cellulose*, which does not act readily with other compounds, while wool and silk contain *nitrogen compounds*, which are much more active. Besides insoluble, colored substances, which enter the fibers of the cloth mechanically, **dyes are usually divided into two classes:**

1. **Direct**, or *substantive*, **dyes.** These unite directly with the fiber to form stable, insoluble compounds. Direct dyes act far more generally with wool and silk than with cotton and linen.

2. **Mordant**, or *adjective*, **dyes.** These require either an acid, like tannic acid, or a substance weakly acid or basic, like the other mordants named, to unite them to the fiber. Thus the fiber, the mordant, and the dye react essentially like acids and bases, producing complex salts, which are the dyed fabrics.

478. Aluminum Salts. — *Aluminum chloride*, AlCl_3 , is soluble in water, and crystallizes with crystal-water ($\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$); but it is so much hydrolyzed that when the water is expelled hydrochloric acid escapes, and aluminum hydroxide remains.



The *anhydrous* chloride is made by letting dry hydrochloric acid gas act upon *hot* aluminum filings. It is a hygroscopic, white powder.

Alums. — *Aluminum sulphate*, $\text{Al}_2(\text{SO}_4)_3$, forms double salts with the sulphates of *univalent* metals, *e. g.*, with *potassium sulphate*, K_2SO_4 ; these double sulphates are called *alums*. The

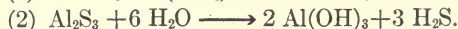
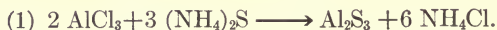
alums crystallize with twenty-four molecules of crystal water. *Potash-alum* is K_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, $24 \text{ H}_2\text{O}$; *silver-alum* is Ag_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, $24 \text{ H}_2\text{O}$. Other *trivalent* elements may replace aluminum. Thus Na_2SO_4 , $\text{Fe}_2(\text{SO}_4)_3$, $24 \text{ H}_2\text{O}$ would be *sodium iron-alum*. *Chrome-alum* is K_2SO_4 , $\text{Cr}_2(\text{SO}_4)_3$, $24 \text{ H}_2\text{O}$.

Aluminum Carbonate and Sulphide. — The electro-positive properties of aluminum are so weak that even its salts with *strong acids*, *e. g.*, the *chloride* and *sulphate*, are readily hydrolyzed. Its salts with weak acids cannot exist in the presence of water, being completely decomposed into the *hydroxide* and the free acid.

When the acid is volatile, it of course escapes. This is the case with the *carbonate*. When aluminum salts are treated with the solution of a carbonate, the products are *aluminum hydroxide* and *carbonic acid*. Hence carbon dioxide escapes.



With the sulphide the result is similar.



479. Porcelain, Stoneware, Etc.

Aluminum silicate, $\text{Al}_2(\text{SiO}_3)_3$, is essentially the substance from which porcelain, etc., are made. In a pure form it is *kaolin*; in an impure form, *clay* (*cf.* § 393).

Porcelain and **china** are made by mixing white kaolin and quartz with more fusible substances, such as *feldspar*, shaping the plastic mixture into form, and "**firing**" it in a pottery **kiln**. The more fusible portion (the feldspar) melts, and cements the whole together. The first heating is at a relatively *low* temperature. The article is then covered with the material of the **glaze**, — a mixture of powdered feldspar and

quartz,—and fired for several days at a high temperature. Porcelain is hard and translucent, and withstands the action of heat and chemicals better than glass, hence it is used for many purposes in chemical laboratories.

Stoneware is *opaque*, for it has not been heated enough to make the feldspar penetrate the kaolin as much as in porcelain.

Earthenware is made from common clay, hardened by heat, but not fused. It is glazed by putting common salt into the furnace at the time of heating. This forms a covering of sodium aluminum silicate over the porous surface. Bricks, tiling, jugs, terra-cotta etc., are examples.

Ultramarine is a blue coloring material, made by melting together *kaolin*, *sodium carbonate*, and *sulphur*. This substance was once very valuable, but thousands of tons of it are now made every year.

480. Exercises.

1. Write the equation for the following reactions:

(a) Aluminum and magnetic iron oxide, heated.

(b) Aluminum chloride and **excess** of barium hydroxide solution.

(c) Decomposition of aluminum sulphate by heat.

(d) Formation of potash-alum.

(e) Hydrolysis of aluminum acetate.

(f) Fusion of aluminum oxide with excess of sodium carbonate.

2. What are the formulas of aluminum phosphate, nitrate, carbide, and nitride? Of calcium metaluminate? Of ammonia-alum?

3. What element is next to aluminum in its abundance? Why is it so much more generally used?

4. How could you distinguish a solution containing an aluminum salt from one containing a calcium salt? A zinc salt?

CHAPTER XXXV.

IRON, NICKEL, AND COBALT.

481. Occurrence of Iron. — Iron is one of the most widely distributed metals, and, next to aluminum, the most abundant (*cf.* § 9). It is found in the soil, in natural waters, in the chlorophyll of plants, and in the hæmoglobin of the blood. Some reaches the earth in *meteorites*, and the spectroscope shows its presence in the sun and stars.

The **principal ores** of iron are **hæmatite** (Fe_2O_3), **magnetite** (Fe_3O_4), **brown iron ore** [$\text{Fe}_2\text{O}_3 \cdot 2\text{Fe}(\text{OH})_3$], and **siderite**, or *spathic iron* (FeCO_3). **Iron pyrites**, FeS_2 , is used for its sulphur (*cf.* § 252).

482. Metallurgy of Iron. — The production of iron is carried out on an enormous scale, since iron is the *most useful metal*. In 1910 the world's production of pig-iron was 64,860,260 **metric tons**. The United States produced 27,303,567 **long tons**. The ores are oxides, or become oxides; hence they are **reduced** by heating them with carbon (coal or coke) and a *flux* (**limestone**; *cf.* §§ 316 and 434). The limestone combines with the silica and aluminum oxide of the ore and coal, and forms **slag**, a glassy mixture of *calcium and aluminum silicates*.

The reduction of iron ore is carried out in *blast-furnaces*.

Blast-Furnace. A blast-furnace (Figs. 88 and 89) is a structure about 100 feet high. The inner walls consist of fire-brick surrounded by brick. The outside is made of sheet-iron. The furnace is charged through the top with coke, ore, and limestone. A double "bell" (A B) permits new charges to be introduced without allowing gases to escape through the top. A blast of hot air is forced into the furnace through pipes, called *tuyères* (T,T), near the bottom. The walls of the furnace just above the tuyères are kept cool by a series of water pipes (W, W). The furnace gases escape through the "downcomers" (C, C) under the "bell." The **iron** collects (in liquid form) in the "crucible," at the bottom of the furnace, and above it the slag. The iron is drawn off through the tap-hole (I) every four to six hours; the slag is run off through (S). The iron is run into molds, forming the bars called "pigs" (whence the name **pig-iron**), or it is transferred, while still molten, to "**converters**" (*cf.* § 487), or furnaces, and made into **steel**. In modern mills the melted iron is poured directly into steel molds. These are brought mechanically under the ladle, chilled in water, and emptied into a nearby car. Such a device is known as a "**pig-machine**."

The operations of the blast-furnace require careful attention. Ores must be analyzed, the composition of flux and reducing agent, and their amounts, must be determined, and the temperature regulated. When once started, blast-furnaces con-

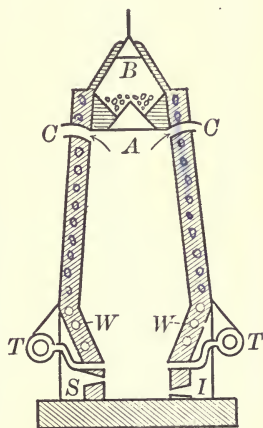


FIG. 88.

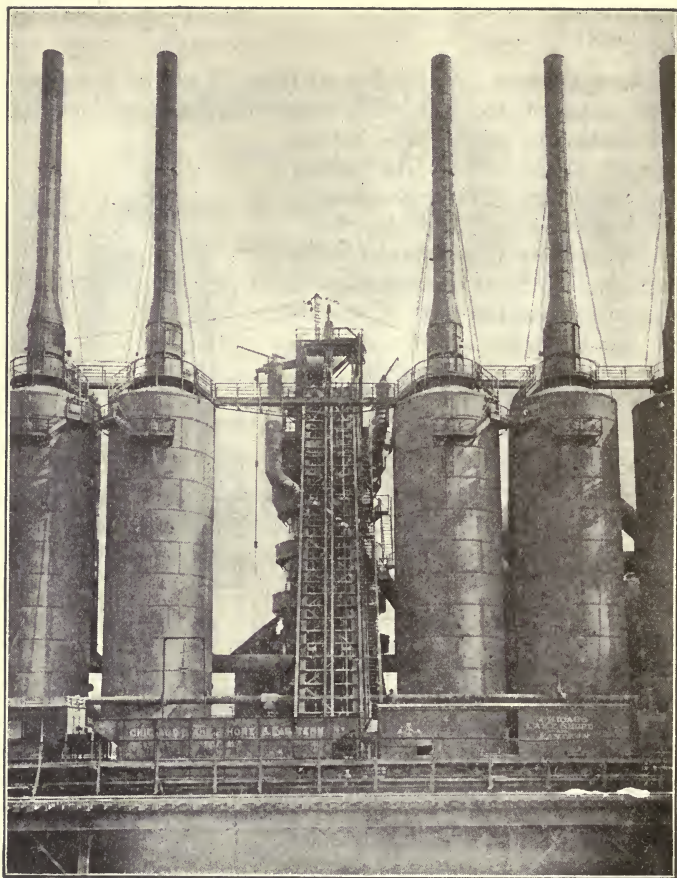


FIG. 89.

A BLAST FURNACE WITH ITS "STOVES" AND CHARGING "SKIP."

tinue "in blast" for months. The largest ones produce 500 tons, or more, of pig-iron a day. **Cast iron** is a form of pig-iron.

The chemical reactions of the blast-furnace are as follows:—

The oxygen of the air-blast first unites with the carbon to form **carbon dioxide**; but this is reduced by the hot carbon higher up to **carbon monoxide** (*cf.* § 286). The gaseous carbon monoxide comes in contact with all parts of the ore, and reduces it.



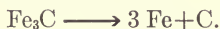
The reaction is **reversible**, but the large excess of carbon monoxide drives it forward (*cf.* § 243). Some of the silica present is reduced to **silicon**. Silicon, sulphur, phosphorus, carbon, and manganese are taken up by the iron, and are, therefore, present in pig-iron. The waste gas that escapes through the downcomers is essentially **producer-gas** (*cf.* § 300), and contains about 25% carbon monoxide. It is used to produce steam for the air-blast engines, or burned in "stoves" (*cf.* Fig. 89) to heat the air itself, or cleaned and used in gas engines for generating power. Blast-furnace slag, when burdened with a calcite stone, is used to make Portland cement (*cf.* § 437).

483. Commercial Iron.—The various grades of commercial iron are *alloys* of iron with carbon and other elements. The carbon may be in **combined** form, as a part of **iron carbide** (Fe_3C), which has 6.6% carbon; or it may be simply **mixed** with the iron, as **graphite** (*cf.* § 272). Any *graphite* present will be left as an insoluble residue when the iron is dissolved in dilute nitric acid of sp. gr. 1.12; but if the carbon is present as *carbide*, it will be partly dissolved and partly given off as *hydrocarbons* (*cf.* § 525). Hydrocarbons are always present in

hydrogen made from acids and iron (*cf.* § 49). **Iron carbide is very hard**, and imparts hardness to iron containing it. The three chief subdivisions of commercial iron are **cast iron, wrought iron, and steel**.

484. Cast Iron. — Cast iron contains from 1.5% to 4% carbon, besides silicon, sulphur, phosphorus, manganese, etc. (*cf.* § 482). It is the lowest-melting form of iron (1050° to 1250° C.). It cannot be welded, forged, or tempered.

Two varieties are distinguished: **gray** cast iron and **white** (or *chilled*) cast iron. If the iron drawn off from the blast-furnace is allowed to cool slowly, most of the iron carbide breaks up, and the carbon is present chiefly as *graphite*.



Hence the cast iron is **gray**. Gray cast iron has a low melting point, and is easily worked with tools. It is made into *castings* by pouring it while melted into sand molds.

When the blast-furnace iron is cooled *very rapidly*, the reaction shown above has not time for its completion, and the cast iron is **white** from the presence of much carbide. White cast iron is very hard and brittle, and hence is not used for castings that are to be *machined*. It is used for making wrought iron and steel, and for *hard* castings.

Spiegeleisen and **ferro-manganese** are cast iron rich in manganese and carbon. They are used to add definite amounts of these elements to wrought iron, thus making steel (§ 486).

485. Wrought Iron. — If the carbon and silicon of cast iron are nearly all removed, the iron becomes tough and malleable, and requires about 1600° C.

to melt it. Wrought iron can be magnetized temporarily. It can also be forged and welded, but not cast or tempered. It has usually 0.06%, or less, of carbon.

Wrought iron may be defined as the product of the "**Puddling**" process. This process consists in heating pig-iron with ferric oxide (iron ore) in an air current upon the hearth of a **reverberatory** furnace (Fig. 86, § 462). The mixture melts, and the impurities of the cast iron are oxidized. The carbon escapes as carbon monoxide, while the oxidized silicon, phosphorus, etc., unite with some of the iron to form a slag. The mass is stirred, or "**puddled**," to permit the air to get at the impurities. As the proportion of the higher melting, pure iron becomes greater, the puddled mass acquires a pasty consistency, and finally it can be made into a ball, or "**bloom**." This is taken from the furnace and hammered with a steam hammer, or *rolled*, to remove most of the slag.

While the structure of cast iron is **crystalline**, that of wrought iron is **fibrous**. Between 900° and 1000° C. wrought iron becomes *plastic*, and while in this condition can be *hammered*, *drawn out* into wire, and *rolled* into sheets or bars. Wrought iron can also be **welded**, that is, pieces can be joined by hammering. The film of oxide that covers the parts to be welded is removed by sprinkling them with borax (*cf.* § 399) or with sand, which convert the oxide into iron borate, or silicate, and permit iron actually to touch iron.

Malleable Iron. When iron castings are covered with iron ore, and heated, the oxygen of the ore combines with much of the carbon of the cast iron, and the castings are converted into a malleable form. Malleable iron is thus a cheap wrought iron.

486. Steel. — Steel is a form of iron containing under 2.2% carbon (practically all of which is in

the combined state) and comparatively small amounts of sulphur and phosphorus. It contains more carbon and silicon than wrought iron, and less than cast iron. Steel containing about 0.2% of carbon is much like wrought iron, and is called **mild steel**. Steel used for buildings ("structural" steel) contains more carbon (0.2% to 0.8%); while tool steel has about 0.8% to 1.5%. The melting point of steel is between the melting points of cast and of wrought iron (about 1475° C.).

Steel combines the advantages of both cast iron and wrought iron; for it may be forged, welded, and cast. It has, besides, the power of being "tempered" to different degrees of hardness (§ 489).

487. Manufacture of Steel. — Steel may be made (1) by removing part of the carbon from cast iron; (2) by adding carbon to wrought iron; and (3) by melting together cast iron and either wrought iron or "blown" iron. Method (1) is rarely used now; method (2) is applied in the **crucible** and **cementation** processes of making steel; method (3) is the basis of the **Bessemer** and the **Open Hearth** (Siemens-Martin) processes. To these must be added the new process of making "**Electric**" steel, in which the electric furnace is employed.

A. The Bessemer Process. The Bessemer process consists essentially in reducing pig-iron in a "converter" to "blown" iron, and then adding enough high-manganese cast iron —

"spiegeleisen"—to bring the proportion of carbon up to the amount wanted.

The **converter** (Fig. 90) is a pear-shaped furnace, 20 feet or more in height, and mounted upon *trunnions* (S) so that it can be inverted. Molten pig-iron is taken directly from the blast-furnace to the converter (§ 482), and a blast of air enters through one trunnion, and is forced up through "*tuyères*" at the bottom (T). This oxidizes the silicon, manganese, and carbon of the pig-iron. The heat produced by this oxidation keeps the iron melted. The manganese of the "*spiegeleisen*" reduces the iron oxide formed during the "*blow*," and is thereby converted into manganese oxide, which separates with the slag.

When a **silica** lining is used in the converter, the process is

called the **acid** Bessemer process. The acid process cannot lower the phosphorus and sulphur content of the pig-iron used. *All Bessemer plants in this country are acid.* In Europe the ores permit the use of the **basic** Bessemer process. In this process the converter lining is *basic* (lime and magnesia), and a pig-iron of very high phosphorus content is required. The reason for this is that the oxidation of the phosphorus furnishes the heat required to keep the metal molten, just as the oxidation of silicon does in the acid process. The slag made in the basic process contains **phosphates**. It is ground up and sold as *fertilizer* ("*Thomas slag*"; cf. § 358).

A converter usually makes 10 to 20 tons of steel at a "*blow*."

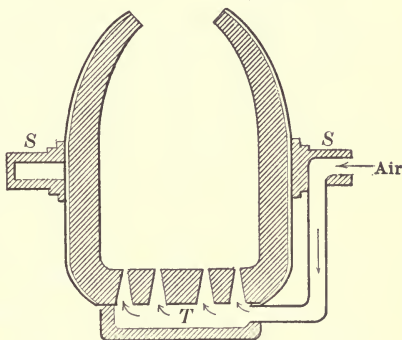


FIG. 90.

The time taken is fifteen to twenty minutes. Bessemer steel contains about 0.35% carbon. It is used for rails, axles, cannon, wire, tin-plate, and structural purposes.

B. Open Hearth Process. In the Open Hearth process pig-iron, wrought iron, or steel scrap is heated with iron oxide (ore) in an open hearth (reverberatory) furnace (*cf.* Fig. 86, § 462). An **oxidizing** gas-flame is used. The furnace consists essentially of a hearth to hold the charge, and a roof to direct the gas-flame down upon it. The gas and air are brought together **hot**, so that the temperature of the flame is very high. The preliminary heating is brought about by passing each of the two gases through fire-brick heated by the products of combustion as they leave the furnace. By the reversal of the direction of the incoming and outgoing furnace gases by means of suitable valves the bricks cooled by the entering gas and air are heated again by the outgoing products of combustion. If the pig-iron used contains much phosphorus, a lining of lime and magnesia may be used (**basic** open hearth furnace); but if select material is available the **acid** process may be used. *Acid open hearth steel is preferable for first-class castings.*

Samples are taken from the furnace at intervals to determine when the per cent of carbon has been lowered sufficiently. The charge is usually from 20 to 100 tons; the process takes from eight to eleven hours. Steel made in this way is very tough and elastic, and suitable for the finest structural work, such as *bridges*, and for machinery bearings, boiler-plate, large guns, etc. Because of the excellent quality of open hearth steel the amount of it produced has gained rapidly upon Bessemer steel, until now (1912) the two are about equal in this country.

C. Crucible and Cementation Steel. The **Crucible** process consists in heating a very pure wrought iron and pure cast iron together in a graphite crucible (*cf.* § 272). The fact that crucible steel is made in a reducing atmosphere, and in the absence of air, makes it remarkably free from oxides and occluded gases.

Because it is cheaper, it is replacing **cementation** steel. In the cementation process wrought iron is packed in charcoal, and heated to redness for several days. As in the crucible process, carbon is gradually absorbed by the metal.

488. Steel Alloys.

Manganese, chromium, nickel, vanadium, tungsten, molybdenum, and silicon are mixed with steel for special purposes, as for imparting great hardness or toughness. Thus nickel steel is used for armor plate, and chrome steel for automobile bearings. Tungsten steel is *self-hardening*; tools made from it require no tempering. To make certain special steels, in which great homogeneity and freedom from oxides and slags are desired, **ferro-titanium** (10% to 15% Ti) is added. The titanium unites readily with nitrogen and with oxygen, giving Ti_3N_4 and TiO_2 , and adds fluidity to the slag.

489. Tempering of Steel. — When steel containing above 0.5% carbon is heated to cherry redness (above 670°C.), and then cooled quickly in water or oil, it becomes hard as glass, and can be given a sharp edge, such as is required for cutting tools. If the hardened steel is reheated, and then allowed to cool *slowly*, it becomes soft. This process is called **annealing**, or “*drawing the temper.*” If, however, the hardened steel is heated up slowly until a film of oxides of a particular color appears upon the surface of the steel, and it is then plunged into water or oil, it will retain a *definite degree of hardness*. This is called **tempering**. The colored films are generally removed from the tempered

article by grinding. They correspond roughly to certain degrees of temperature, as is shown in the following table:

Temperature.	Color.	Use of Steel.
610° C.	Blue-black.	Saws.
530°—570°.	Blue.	Watch Springs.
520°.	Purple.	Table Knives.
490°—510°.	Brown.	Shears.
470°.	Bright Yellow.	Pocket Knives.
430°—450°.	Pale Yellow.	Razors.

490. Causes of the Behavior of Iron and Steel. — Two things must be kept in mind in studying the behavior of iron and steel:

(1) Pure iron exists in several allotropic forms, and only **one** of these can dissolve carbon (as carbide) in any considerable amount.

(2) Iron carbide imparts hardness to cast iron and steel, but decomposes below 670° C.



The forms of iron and their properties are: —

A. Stable below 765° C.	Magnetic.	Dissolves little Fe_3C .
B. Stable 765°—890°.	Not Magnetic.	Dissolves little Fe_3C .
C. Stable above 890°.	Not Magnetic.	Dissolves Fe_3C .

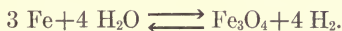
When iron of form **C**, containing Fe_3C , is cooled *slowly*, it passes through **B** into **A**, and below 670° C. the carbide breaks

up into pure (wrought) iron and *graphite*. But **sudden** cooling does not allow time for these changes. Chilled cast iron (§ 484) is a solid solution of Fe_3C in iron of form *C*. Hard steel represents a similar condition, but it has less carbide, and practically no sulphur and phosphorus. When the steel is gradually re-heated (tempered), there is a partial change of iron *C* into *A*, and a partial decomposition of the iron carbide; hence the steel is softened. The metals present in steel alloys are used, not only because of their own peculiar properties, but also because they prevent, or retard, the change of iron *C* into *A*. Since the properties of an iron alloy depend both upon the proportions of pure iron, iron carbide, and graphite present, and also upon their **condition** in the mixture, the best way to study iron is to polish a section of it, to etch the polished face with an acid, and then to examine it carefully with the microscope. The constituents and their condition can thus be determined.

491. Properties of Iron. — Pure iron is rare; it melts at about 1800°C . The purest commercial form is wrought iron; this is a fairly good conductor.

Soft, i. e., *wrought*, iron may be magnetized *temporarily*, but soon loses the magnetism; steel is not so easily magnetized, but becomes a *permanent* magnet.

At red heat iron decomposes water vapor.



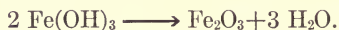
When iron is burned in oxygen the same oxide results (*cf.* § 24). In dry air iron does not change, but in the presence of moisture and carbon dioxide it *rusts*. Iron rust is a mixture of *ferric oxide* (Fe_2O_3) and *ferric hydroxide*, $\text{Fe}(\text{OH})_3$. Iron reacts easily

with dilute acids, forming **ferrous** salts, in which iron is *bivalent*. These are readily oxidized, even by the oxygen of the air, to **ferric** salts, containing *trivalent* iron (*cf.* § 181). Ferric salts are reduced by hydrogen sulphide, stannous chloride, and nascent hydrogen to the ferrous state. Solutions containing ferrous ions are pale green; those of ferric ions are yellow or light brown.

492. Oxides and Hydroxides of Iron.

Ferrous oxide (FeO) is not easily prepared or kept. It may be made by reducing ferric oxide with hydrogen at 300°C. , but on exposure to air it is oxidized at once.

Ferric oxide, Fe_2O_3 , is found in enormous masses (*hæmatite*). It may be made by heating *ferric hydroxide* or *ferrous sulphate*.



Ferrous-ferric oxide, Fe_3O_4 , is called the “magnetic oxide” of iron; it occurs as *magnetite*. It is sometimes found as *lodestone*, a natural magnet. Iron may be kept from rusting by exposing it while red hot to steam; the resulting layer of the black oxide, Fe_3O_4 , protects the remainder of the metal. Iron so coated is **Russia iron**.

Ferrous hydroxide, Fe(OH)_2 , is formed when an alkali in solution is added to the solution of a *ferrous* salt. It is usually *green*, but soon becomes brown where air is in contact with it. In the absence of air it is white.

Ferric hydroxide, Fe(OH)_3 , is made by adding an alkali or ammonia water to the solution of a *ferric* salt. It forms a flaky, red-brown precipitate.

493. Iron Sulphides.

Ferrous sulphide, FeS (*cf.* § 250), is a black solid made by heating a mixture of sulphur and iron, and by adding an alkali sulphide to a *ferrous* salt solution.

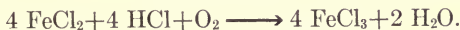


Hydrogen sulphide precipitates only a *trace* of ferrous sulphide from a ferrous salt (*cf.* § 255), and *reduces* a ferric salt to the ferrous state. Ammonium sulphide also reduces ferric ions to ferrous ions, and thus precipitates FeS from both ferrous and ferric salts.

Iron pyrites (FeS_2) has the color of brass, and is called "fool's gold." For its behavior when heated, see § 252.

494. Iron Chlorides.—Ferrous chloride, FeCl_2 , is made by passing hydrogen chloride over hot iron. A solution of it results when iron is treated with the acid. Like all *ferrous* compounds it is oxidized easily to the *ferric* condition. The anhydrous salt is white.

In the presence of hydrochloric acid the air oxidizes it to *ferric chloride*.



If no acid is present, part of the iron is oxidized to ferric salt, and part to *ferric hydroxide* (rust).



Ferric chloride, FeCl_3 , is formed in solution by passing *chlorine* into ferrous chloride solution, or by treating iron with *aqua regia*, and evaporating *repeatedly* with hydrochloric acid. The anhydrous

salt is made by passing chlorine over red-hot iron. It looks like maple-sugar.

495. Iron Sulphates. — A solution of *ferrous sulphate*, FeSO_4 , results when iron reacts with dilute sulphuric acid. The crystals known as *green vitriol* or “copperas” are $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$. Green vitriol is used in making inks, in dyeing, and as a deodorizer. **Common writing ink** is **ferric tannate** (*cf.* § 546), suspended in water by means of dissolved gum arabic or dextrin. It is made by treating an extract of nut-galls with ferrous sulphate. The resulting *ferrous* tannate is oxidized by the air. The *double salt*, *ferrous ammonium sulphate*, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6 \text{H}_2\text{O}$, is much less easily oxidized than ferrous sulphate alone.

Ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, is made, in solution, by oxidizing ferrous sulphate with nitric acid in the presence of sulphuric acid.

496. Ferro- and Ferri-cyanides.

Potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, is called “yellow prussiate (i. e., *cyanide*, *cf.* § 290) of potassium.” It is a yellow, crystalline solid made by heating together potash, iron, and animal matter, such as hoofs and horns. With a ferric salt it gives **Prussian blue**, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. With a ferrous salt it gives a **white** precipitate of $\text{K}_2\text{FeFe}(\text{CN})_6$. **Potassium ferri-cyanide**, $\text{K}_3\text{Fe}(\text{CN})_6$, is made by oxidizing the ferrocyanide with chlorine. It is a red, crystalline solid. With a **ferrous** salt it gives **Turnbull’s blue**, $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$; with a **ferric** salt, a *brown solution* of $\text{Fe}(\text{CN})_3$.

The divided formula, $\text{Fe}(\text{CN})_2 \cdot 4 \text{KCN}$, shows that iron is *ferrous* in potassium ferrocyanide (ferro- means *ferrous*). In the *ferricyanide*, $\text{Fe}(\text{CN})_3 \cdot 3 \text{KCN}$, iron is in the *ferric* condition.

Ferric thiocyanate, $\text{Fe}(\text{SCN})_3$, is present in the blood-red solution produced by adding potassium thiocyanate, KSCN (i. e., *SCN ions*; cf. § 426), to a ferric salt. The corresponding ferrous salt is colorless.

Blue-print paper contains a *ferric* salt and potassium ferricyanide (cf. § 466). Exposure to light *reduces* the ferric salt to the ferrous state, and Turnbull's blue results. Washing removes the unchanged materials.

Both Prussian blue and Turnbull's blue are soluble in alkalis, because decomposed into iron hydroxides and ferro- or ferricyanides.

497. Nickel. — Nickel is found with iron in meteorites. A silicate of nickel and magnesium, *garnierite*, found in New Caledonia, is its chief ore. *Niccolite* is NiAs , and *nickel glance*, NiAsS . The metal may be obtained by reducing its oxide with hydrogen, carbon, or aluminum (cf. § 308). Like iron, nickel is **magnetic**. It is used to plate other metals to protect them from the atmosphere; also to make **alloys**, such as German silver, nickel steel, and the United States five-cent piece.

Nickel forms nickelous oxide and hydroxide, and **nickelous** salts, in which the metal is *bivalent*. It also forms **nickelic** oxide (Ni_2O_3) and hydroxide, $\text{Ni}(\text{OH})_3$; but *no nickelic salts*. Nickel reacts very slowly with hydrochloric and sulphuric acids, but readily with nitric acid. Nickelous oxide and hydroxide are green, insoluble solids. Nickelic oxide and hydroxide are black. Nickelous salts are green in solution. The sulphate crystallizes

as $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$; the chloride, as $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$. The sulphide, NiS , is precipitated by alkali sulphides. It is black. The cyanide, $\text{Ni}(\text{CN})_2$, dissolves in an excess of potassium cyanide, giving $\text{K}_2\text{Ni}(\text{CN})_4$.

Nickel carbonyl, $\text{Ni}(\text{CO})_4$, is formed when carbon monoxide is passed over finely divided nickel at the ordinary temperature. It is a colorless liquid boiling at 43°C . It is dissociated at $150^\circ - 180^\circ$.



Nickel carbonyl is used to extract nickel from its ores, and to separate nickel from cobalt, which does not form a similar compound. Iron forms the carbonyls $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$. In the oxidizing flame nickel compounds form a **brown** borax bead.

498. Cobalt. — Cobalt is found as *cobaltite*, CoAsS , and *smaltite*, CoAs_2 , associated with the corresponding nickel ores. Roasting produces the *oxide*, and this is reduced with hydrogen or charcoal. The metal is white, with a pinkish cast, while nickel is yellowish. Like nickel and iron it is magnetic. It reacts slowly with all acids but nitric acid.

Cobalt forms the oxides CoO , Co_2O_3 , and Co_3O_4 . The first corresponds to **cobaltous**, the second to **cobaltic** salts. Cobaltous salt solutions, *i. e.*, Co^{++} ions, are *pink*. The molecular salts are *blue*. The *chloride* crystallizes as $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$, the *nitrate* as $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, and the *sulphate* as $\text{CoSO}_4 \cdot 7 \text{H}_2\text{O}$. *Cobalt silicate* is **smalt**, a deep-blue pigment for coloring glass and porcelain. The *aluminate*, $\text{Co}(\text{AlO}_2)_2$, is *Thénard's blue*. The change of the hydrated, pink cobalt salts to the anhydrous, blue ones is the basis of "sympathetic inks," which are practically

invisible under the ordinary (damp) atmospheric conditions, but become blue, and visible, when dried.

Sodium hydroxide and cobaltous salts give *blue basic salts*, which are converted, by heating, into *red* $\text{Co}(\text{OH})_2$. The *cyanide*, $\text{Co}(\text{CN})_2$, is soluble in an excess of potassium cyanide, giving $\text{K}_4\text{Co}(\text{CN})_6$. This corresponds to $\text{K}_4\text{Fe}(\text{CN})_6$. It is easily oxidized, even by the air, to $\text{K}_3\text{Co}(\text{CN})_6$.

A cobaltous salt reacts with *potassium nitrite* and *acetic acid* to give a yellow precipitate of $\text{K}_3\text{Co}(\text{NO}_2)_6$, *i. e.*, $\text{Co}(\text{NO}_2)_3 \cdot 3\text{KNO}_2$. This is *potassium cobaltic nitrite*. Nickel forms no salts resembling either $\text{K}_3\text{Co}(\text{CN})_6$ or $\text{K}_3\text{Co}(\text{NO}_2)_6$. Both nickel and cobalt give *complex positive ions* with excess of ammonia water (*cf.* §§ 459 and 465). The salts of these complex ions are **soluble**. Iron forms no such compounds. Cobalt compounds color the borax and metaphosphate beads **blue**.

499. Exercises.

1. Write the equations for the following reactions: —

- (a) Limestone and silica; limestone and aluminum oxide.
- (b) Iron carbide and hydrochloric acid.
- (c) Ferric oxide and borax; ferric oxide and sand.
- (d) Ferric chloride and hydrogen sulphide.
- (e) Ferric sulphate and nascent hydrogen.
- (f) Hydrolysis of ferric nitrate.
- (g) Ferrous sulphate, dilute sulphuric acid, and nitric acid.
- (h) Ferric salt and ammonia water.
- (i) Oxidation of ferrous hydroxide (moist) by air.
- (j) Ferrous salt and ammonium sulphide.
- (k) Ferric salt and ammonium sulphide (stages).
- (l) Iron and aqua regia.
- (m) Ferrous salt and potassium ferricyanide.
- (n) Ferrous salt and potassium ferrocyanide.
- (o) Ferric salt and potassium ferricyanide.
- (p) Ferric salt and potassium ferrocyanide.

(q) Ferric salt and ammonium thiocyanate.

(r) Prussian and Turnbull's blue with caustic soda.

2. Write the equations for the reactions by which the following are prepared from cobalt nitrate: cobalt hydroxide, oxide, and cyanide; potassium cobaltocyanide, potassium cobalticyanide.

3. Write the equations for the preparation of the following from nickel nitrate: nickel oxide, hydroxide, sulphate, and sulphide; potassium nickel cyanide.

4. Give all the ways in which iron, nickel, and cobalt are alike. In what respects do they differ? How would you distinguish between ferrous, ferric, cobaltous, and nickelous ions in solution?

CHAPTER XXXVI.

MANGANESE AND CHROMIUM.

500. Manganese. — Manganese occurs as the **dioxide** (MnO_2), which is **pyrolusite**; also as **hausmannite** (Mn_3O_4) and **manganese spar** (MnCO_3). The metal is made by reducing its oxides with aluminum (*cf.* § 308). It is hard, brittle, steel-gray, and non-magnetic. Manganese melts at about 1300°C. , rusts in moist air, and replaces the hydrogen of the ordinary dilute acids, giving **manganous** salts. Manganese is used in making steel (*cf.* § 484).

501. Manganese Compounds. — The oxides of manganese have the formulas $\text{Mn}^{\text{II}}\text{O}$, $\text{Mn}_2^{\text{III}}\text{O}_3$, Mn_3O_4 , $\text{Mn}^{\text{IV}}\text{O}_2$, $\text{Mn}^{\text{V}}\text{O}_3$, and $\text{Mn}_2^{\text{VII}}\text{O}_7$. All are solids but the last, which is a dark liquid.

The only decidedly basic oxide is *manganous oxide* (MnO). This is a green, amorphous solid, formed when the carbonate (MnCO_3) is heated in absence of air. The air oxidizes it to Mn_3O_4 . Manganous hydroxide, $\text{Mn}(\text{OH})_2$, is precipitated as a white solid, insoluble in an excess of the strong bases; it has no acid properties. It is easily oxidized by the air to the dark *hydrate of manganic oxide*, $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The stable manganese salts are all **manganous**. When the higher oxides of manganese are treated with acids, they lose all the oxygen they contain in excess of that represented by the formula MnO . The excess of

oxygen is either given off as such, as is the case when manganese dioxide is heated with concentrated sulphuric acid, or the oxygen is used in oxidizing the acid, as is the case with hydrochloric acid. The resulting **salts** are **manganous** (cf. §§ 115 and 138). The common manganous salts are pink, crystalline, soluble solids. **Manganous sulphate** crystallizes with different proportions of water ($\text{MnSO}_4 \cdot 7 \text{H}_2\text{O}$, $5 \text{H}_2\text{O}$, or $4 \text{H}_2\text{O}$). The **chloride** is $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$. The **carbonate** is a white, insoluble solid. The **sulphide** (MnS) is precipitated as a light-pink solid by soluble metal sulphides, but not by hydrogen sulphide (cf. § 255). The oxide Mn_3O_4 is formed when the other oxides are heated in air (cf. § 22). The **dioxide** is the most important manganese compound. It is used to prepare manganese, chlorine, and oxygen, and to decolorize glass. It makes glass colorless by neutralizing the green color produced by the iron present in the materials used (cf. § 394). Manganese dioxide is the anhydride of the unstable compounds H_4MnO_4 and H_2MnO_3 . These are the "ortho" and the "meta" form of **manganous acid** (cf. § 355). *Calcium manganite* is CaMnO_3 . *Hausmannite* is **manganous manganite**, Mn_2MnO_4 . In the *oxidizing flame* manganese compounds form an **amethyst-colored** borax bead. In the *reducing flame* it is colorless.

502. Manganates and Permanganates. — *Manganese trioxide* (MnO_3) is the anhydride of *manganic acid*, H_2MnO_4 , and the *heptoxide* (Mn_2O_7) is the anhydride of *permanganic acid*, HMnO_4 . Manganic acid is not known in the free state. Its salts, e. g., K_2MnO_4 , are hydrolyzed in solution. Manganate solutions, i. e., MnO_4^- ions, are *green*. **Permanganic acid** is a strong acid. It can be prepared (as a hydrate), but is unstable. Permanganate ions (MnO_4^-) are *purple*.

A **manganate** is formed by fusing together a manganese compound, a **base** (or alkali carbonate), and an **oxidizing agent**, such as potassium nitrate or chlorate. If *manganous sulphate* is used, the equations are: —

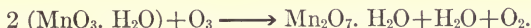
- (1) $\text{MnSO}_4 + \text{K}_2\text{CO}_3 \longrightarrow (\text{MnCO}_3) + \text{K}_2\text{SO}_4.$
- (2) $(\text{MnCO}_3) \longrightarrow (\text{MnO}) + \text{CO}_2 \uparrow.$
- (3) $\text{KClO}_3 \longrightarrow \text{KCl} + 3 \text{O}.$
- (4) $(\text{MnO}) + 2 \text{O} \longrightarrow (\text{MnO}_3).$
- (5) $\text{K}_2\text{CO}_3 + \text{MnO}_3 \longrightarrow \text{K}_2\text{MnO}_4 + \text{CO}_2 \uparrow.$

If MnO_2 is used, equations (1) and (2) are omitted.

Permanganates are formed by the oxidation of manganates. Thus *ozone* converts potassium manganate into the permanganate.

- (1) $\text{K}_2\text{MnO}_4 + 2 \text{HOH} \rightleftharpoons 2 \text{KOH} + \text{H}_2\text{MnO}_4.$
- (2) $2 \text{H}_2\text{MnO}_4 + \text{O}_3 \longrightarrow 2 \text{HMnO}_4 + \text{H}_2\text{O} + \text{O}_2.$
- (3) $\text{KOH} + \text{HMnO}_4 \longrightarrow \text{KMnO}_4 + \text{H}_2\text{O}.$

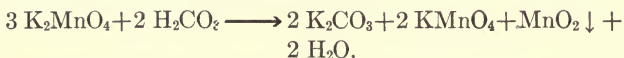
The best way to represent the relation between manganic and permanganic acids is to consider them as **hydrates of their anhydrides**. It is thus made plain that the change is an oxidation of MnO_3 to Mn_2O_7 . Equation (2) then becomes: —



Carbon dioxide also converts a manganate solution into one of permanganate; but some of the manganate is reduced to manganese dioxide to provide the necessary oxygen.

- (1) $3 \text{K}_2\text{MnO}_4 + 6 \text{HOH} \rightleftharpoons 6 \text{KOH} + 3 \text{H}_2\text{MnO}_4$ [*i. e.*, $3 (\text{MnO}_3 \cdot \text{H}_2\text{O})$].
- (2) $3 (\text{MnO}_3 \cdot \text{H}_2\text{O}) \longrightarrow \text{Mn}_2\text{O}_7 \cdot \text{H}_2\text{O} + \text{MnO}_2 \downarrow + 2 \text{H}_2\text{O}.$
- (3) $4 \text{KOH} + 2 \text{H}_2\text{CO}_3$ (*i. e.*, $2 \text{H}_2\text{O} + 2 \text{CO}_2$) $\longrightarrow 2 \text{K}_2\text{CO}_3 + 4 \text{H}_2\text{O}.$
- (4) $2 \text{KOH} + 2 \text{HMnO}_4 \longrightarrow 2 \text{KMnO}_4 + 2 \text{H}_2\text{O}.$

If we omit the formulas appearing on **both** sides of the equation, the "complete" equation is: —



Other dilute acids may be used in place of the carbonic acid.

Potassium permanganate separates from solution as greenish-black prisms. Its solution is deep purple. When the solid is heated, it is decomposed.

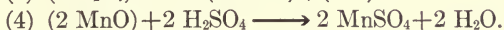
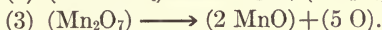
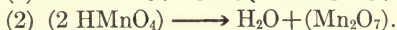
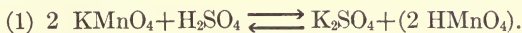


A crude permanganate solution, made from sodium manganate and dilute sulphuric acid, is used as a disinfectant.

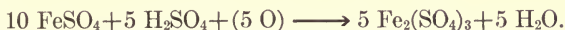
503. Oxidation by Potassium Permanganate. — Potassium permanganate is used for oxidizing purposes under *acid*, *neutral*, and *alkaline* conditions. Oxidation in **acid solution** is most common. As the oxygen is used up, the purple color disappears, because the resulting manganous salt solution is colorless. This fact makes it possible to use potassium permanganate solution in **volumetric analysis**. To determine the amount of some reducing agent, *e. g.*, **oxalic acid**, in a solution we need only find out how much potassium permanganate solution, of known concentration, the oxalic acid can decolorize. The concentrations of solutions of *formic acid*, *ferrous salts*, *sulphurous acid*, *hydrogen peroxide*, etc., can be obtained in the same way. In **acid**

solutions **2 gram-molecular weights** of permanganate give **5 gram-atomic weights** of oxygen.

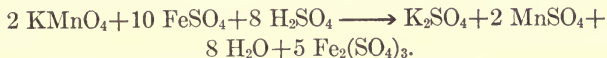
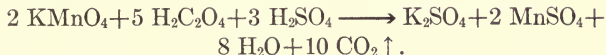
The following are the *partial* equations for the action of acidified permanganate with oxalic acid.



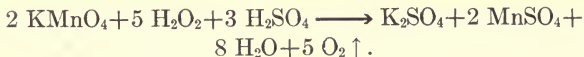
For the oxidation of FeSO_4 to $\text{Fe}_2(\text{SO}_4)_3$ equation (5) becomes:—



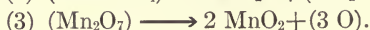
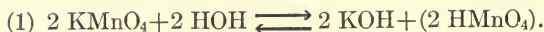
In complete form these equations are:—



Hydrochloric acid both liberates permanganic acid and reduces it; HCl is, therefore, substituted for H_2SO_4 in equations (1) and (4), and for $\text{H}_2\text{C}_2\text{O}_4$ in equation (5). Potassium permanganate and *hydrogen peroxide* **reduce each other** (*cf.* § 340) with liberation of oxygen.



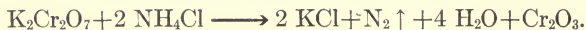
When potassium permanganate is used in **neutral** or **alkaline** solution, **2 gram-molecular weights** of the permanganate give **3 gram-atomic weights** of available oxygen.



504. Chromium. — Chromium is a comparatively rare element, which occurs as *chromite*, $\text{Fe}(\text{CrO}_2)_2$, *i. e.*, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. The metal is prepared by reducing chromic oxide, Cr_2O_3 , with aluminum (*cf.* § 308). It is steel-gray, very hard, and very difficult to fuse. It is used in the alloy “chrome-steel” (*cf.* § 488). “Chromium” is from the Greek *chroma*, meaning “color.”

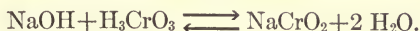
505. Chromium Oxides and Hydroxides. — Chromium forms *chromous oxide* ($\text{Cr}^{\text{II}}\text{O}$), *chromic oxide* ($\text{Cr}_2^{\text{III}}\text{O}_3$), and *chromium trioxide* ($\text{Cr}^{\text{VI}}\text{O}_3$). *Chromous* salts are derived from CrO ; *chromic* salts from Cr_2O_3 . Chromium trioxide is *chromic anhydride* (*cf.* § 507).

Chromic oxide is the pigment “chrome-green.” It is made by dehydrating its hydroxide, $\text{Cr}(\text{OH})_3$, and by heating a mixture of ammonium chloride, potassium dichromate, and sodium carbonate. The last need not appear in the equation.



Chromic hydroxide, $\text{Cr}(\text{OH})_3$, is formed as a green precipitate when an alkali hydroxide, carbonate or sulphide is added to a chromic salt. It is a **weak base**, like aluminum hydroxide; hence its carbonate and sulphide are completely *hydrolyzed* by water (*cf.* § 478). It is also a **weak acid**, and dissolves in an excess of a strong base, forming a **chromite**. Chromites form

green solutions. They are derived from the hydroxide, H_3CrO_3 , or the "meta" form, HCrO_2 (cf. §§ 355 and 501).



When the solution is boiled, it is hydrolyzed, giving a precipitate of the hydroxide.

506. Chromous and Chromic Salts. — Chromous salts are derived from the hydroxide, $\text{Cr}(\text{OH})_2$, and the oxide, CrO . These are basic, like the corresponding ferrous and manganous compounds. Chromous ions (Cr^{++}) are *blue*. Chromous salts are so readily oxidized to the chromic state that they are hard to prepare. In this they resemble ferrous but not manganous salts. The chief **chromic** salts are the *chloride*, CrCl_3 , the *sulphate*, $\text{Cr}_2(\text{SO}_4)_3$, and *chrome-alum*, $\text{K}_2\text{Cr}_2(\text{SO}_4)_4 \cdot 24 \text{H}_2\text{O}$. Chromium compounds give an emerald-green borax or metaphosphate bead.

Chromic chloride is a lavender-colored solid when anhydrous. It is obtained when chlorine is passed over a mixture of chromic oxide and carbon.



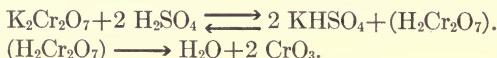
In solution, chromic chloride is green, and can be obtained in green crystals, $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$.

Chromic sulphate forms a violet solution with *cold* water. When the solution is evaporated *at the ordinary temperature*, reddish-violet crystals [$\text{Cr}_2(\text{SO}_4)_3 \cdot 15 \text{H}_2\text{O}$] separate out. If the solution is heated, it becomes *green*, and on evaporation gives a sticky, dark mass. *Chrome-alum* behaves in the same way.

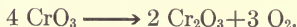
Chrome-alum forms large, octahedral, violet-colored crystals (*cf.* § 478). It is formed when potassium dichromate is used as an oxidizing agent in the presence of sulphuric acid (*cf.* § 509). Chrome-alum is used in dyeing and tanning (*cf.* § 477).

507. Chromium Trioxide. — Chromium trioxide resembles the higher oxides of manganese in being the **anhydride** of acids. *Chromic acid* is H_2CrO_4 (or $\text{H}_2\text{O} \cdot \text{CrO}_3$), and *dichromic acid* is $\text{H}_2\text{Cr}_2\text{O}_7$ (or $\text{H}_2\text{O} \cdot 2 \text{CrO}_3$). Chromium is in the same periodic group with sulphur (*cf.* § 383); but while sulphuric acid is stable, chromic acid is too unstable to be prepared. Its solution gives the anhydride when evaporated. This is often called chromic acid.

Chromium trioxide is formed in bright-red crystals when concentrated sulphuric acid is added to a saturated solution of potassium dichromate.



It is a powerful oxidizing agent, owing to the ease with which it breaks down into chromic oxide and oxygen.

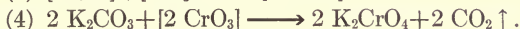
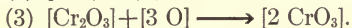
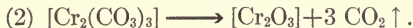


It sets fire to alcohol dropped upon it, destroys organic substances, such as paper, and oxidizes hydrochloric acid. When it is heated, oxygen is set free.

508. Chromates and Dichromates. — Chromium compounds are made from the chromates or dichromates (*cf.* §§ 504 to 507). Potassium chromate is

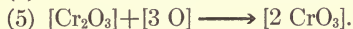
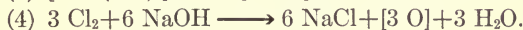
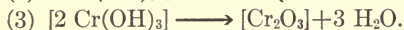
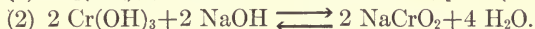
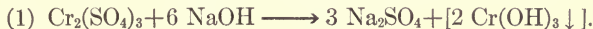
made from *chromite*, $\text{Fe}(\text{CrO}_2)_2$, or $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, by roasting it with potassium carbonate and quicklime in the oxidizing flame of a reverberatory furnace (*cf.* § 462). On a small scale, chromite is heated with a mixture of potassium nitrate and carbonate.

The methods given show that we convert a chromium compound to a *chromate* by *oxidizing* it in the presence of a **base**. For $\text{Cr}_2(\text{SO}_4)_3$ the equations are:—



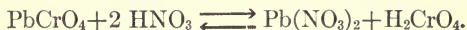
For the preparation of a chromate from chromite, equations (1) and (2) are omitted.

Oxidation of a chromic compound to a chromate may also take place *in solution*, as by adding chlorine to an *alkali chromite*, *i. e.*, to chromic hydroxide dissolved in an *excess* of alkali.



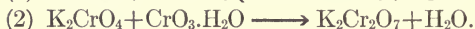
In making the **complete** equation, the reversible equation (2) is omitted.

Chromates are generally *yellow*. Those of the alkalis are soluble. The insoluble chromates react with dilute acids, giving soluble products. Lead chromate is the pigment “chrome-yellow.”

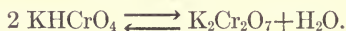


Potassium dichromate, $K_2Cr_2O_7$, forms large, red crystals, which are soluble. *Sodium dichromate* is often used in place of the potassium salt, because it is more soluble. Both chromates and dichromates are used in dyeing, in calico-printing, and as oxidizing agents. Potassium dichromate is used in photography and to prevent polarization in the "dichromate" battery.

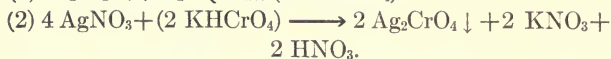
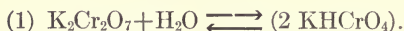
When a chromate solution is treated with an acid, a **dichromate** is formed. The color is changed to *red*, owing to the formation of Cr_2O_7 ions. Conversely, a base changes a dichromate to a chromate. We can understand the relation of chromates to dichromates better if we write the formulas of the corresponding acids as **hydrates of their anhydrides**, just as we did with the manganese acids (cf. § 507).



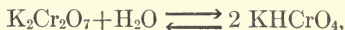
Potassium dichromate is thus an **acid salt**, but the form $KHCrO_4$ loses water.



While the reverse action, producing $KHCrO_4$, is small, it is appreciable; so that when potassium dichromate solution is added to the solution of a ionic metal that forms an *insoluble* chromate, the **chromate** of the metal is precipitated.



When a base is added to a dichromate, the reversible equation,

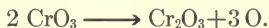


is made **complete**, by the replacement of the H of KHCrO_4 by a metal. Hence a **chromate** is formed.

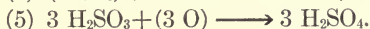
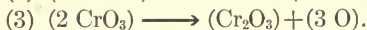
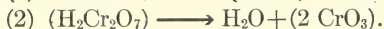


509. Oxidation by Chromates and Dichromates. —

When chromic compounds are oxidized to chromates, a base is added, as well as an oxidizing agent; hence when chromates or dichromates are used as **oxidizing agents**, *i. e.*, are *reduced*, the operation is carried out **in acid solution**. The fundamental reaction is the change of chromium trioxide to chromic oxide, with loss of oxygen (*cf.* § 507).



The oxygen unites with the reducing agent, while the chromic oxide reacts with the acid, giving a *chromic salt*. The reaction between *potassium dichromate*, *dilute sulphuric acid*, and *sulphurous acid* (sulphur dioxide) is as follows: —



When the solution is evaporated at the ordinary temperature, chrome-alum is formed (*cf.* § 506).

When **alcohol** is the reducing agent, equation (5) is: —



Hydrochloric acid and potassium dichromate give **chlorine** (*cf.* § 116). In this case, HCl takes the place of H_2SO_4 in equations (1) and (4), and of H_2SO_3 in equation (5).

Hydrogen peroxide oxidizes a dichromate to **perchromic acid**, which is extracted from water solution by ether, and colors the ether *blue* (cf. § 340).

510. Exercises.

1. Give the equations for: —

- (a) Heating MnO and MnO_2 in air.
- (b) Oxidation of $\text{Mn}(\text{OH})_2$ by the air.
- (c) Action of MnO_2 with concentrated H_2SO_4 . With HCl .

2. Give partial and complete equations for: —

- (a) Heating a mixture of $\text{Mn}(\text{NO}_3)_2$, KOH , and KClO_3 .
- (b) Treating the following with KMnO_4 in dilute sulphuric acid solution: formic acid, sulphurous acid, ferrous chloride.
- (c) Action of HCl upon solid KMnO_4 .
- (d) Preparation of Cr_2O_3 from $\text{K}_2\text{Cr}_2\text{O}_7$ and NH_4Cl (§ 505).

Remember that $\text{NH}_4\text{Cl} \longrightarrow \text{NH}_3 + \text{HCl}$.

- (e) Reaction between solutions of $\text{Cr}(\text{NO}_3)_3$ and K_2CO_3 .
- (f) The same for solutions of $\text{Cr}_2(\text{SO}_4)_3$ and $(\text{NH}_4)_2\text{S}$.
- (g) Action of HCl upon solid $\text{K}_2\text{Cr}_2\text{O}_7$.
- (h) Reaction when H_2S is passed through a dilute sulphuric acid solution of KMnO_4 . Through one of $\text{K}_2\text{Cr}_2\text{O}_7$.
- (i) Preparation of K_2CrO_4 from CrCl_3 . From $\text{Cr}_2(\text{SO}_4)_3$.

3. Exactly 20 c.c. of a solution containing 15.8 g. of KMnO_4 per liter were needed to react completely with some H_2O_2 solution. How much H_2O_2 was there?

4. If 0.056 g. of iron is dissolved in dilute sulphuric acid, how much KMnO_4 is required to oxidize the resulting FeSO_4 to the ferric state?

5. How could you prepare lead, calcium, and silver chromates? Give the equations.

6. What is meant by the "polarization" of a voltaic cell? To what is it due? How does $\text{K}_2\text{Cr}_2\text{O}_7$ prevent it? What chromium compound is formed in the "dichromate" battery?

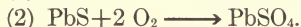
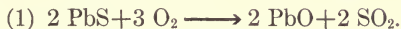
CHAPTER XXXVII.

LEAD, TIN, AND PLATINUM.

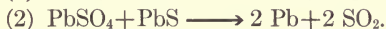
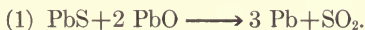
511. Occurrence and Preparation of Lead. —

Lead occurs chiefly as *galena*, PbS , and is obtained from it by the following processes: —

(1) If the ore is of high grade, it is first roasted in a reverberatory furnace (*cf.* § 462). By this operation part of the ore is changed to the *oxide*, PbO , and part to the *sulphate*, PbSO_4 , while some remains unchanged.



After the oxidation has gone far enough, the furnace doors are closed, and the mixture is heated without the admission of more air. The lead oxide and sulphate then react with the unchanged sulphide as follows: —



(2) If the ores are poor, they are reduced in a blast-furnace, or heated with iron.



(3) If there is enough silver to pay for its extraction (**base bullion**; *cf.* § 462), the **Parkes** process is used.

(4) Lead may also be made by the electrolysis of a mixture of galena and dilute sulphuric acid. About 970,000 tons of lead were produced in 1910; 372,000 tons in the United States.

512. Properties and Uses. — Lead is a soft, blue-gray metal, having a high luster which is soon tarnished by oxidation. The corrosion does not penetrate, as with iron. Lead is not very malleable, or ductile, but it can be rolled into sheets, and forced, while hot, through steel dies, forming lead pipe. It melts at 327°C .

Lead (*i. e.*, lead ions, Pb^{++}) is readily displaced from the solutions of its salts by such metals as zinc and iron (*cf.* § 180). It often separates in a branching, crystalline form, known as a **lead tree**. Nitric acid reacts readily with lead, forming the *nitrate*. Dilute sulphuric attacks it very slowly; the hot, concentrated acid acts as upon copper (*cf.* § 265). When lead is boiled with concentrated hydrochloric acid, hydrogen is formed, but very slowly. Many organic acids, *e. g.*, acetic acid, act upon it, in the presence of air, to form soluble salts.

All compounds of lead are poisonous. When even *small* amounts of lead are taken *regularly* into the body, as in drinking water, the lead accumulates until it causes sickness. Painters are subject to “painter’s colic,” because of the lead compounds in paint. Lead is almost unaffected by pure water, if air is not present; but air and soft water together produce lead hydroxide, which is slightly soluble. The presence of carbon dioxide makes lead react even more readily with water. *Hard water* acts upon lead very slightly, because a coating of lead carbonate and sulphate soon protects it from further action. Great care should be exercised in using water that has run through new lead pipes.

Besides being used for conveying water, lead pipes are used as sheaths for the cables of telephone wires. In sheet form, the metal is used to line the “leaden chambers” (*cf.* § 262), and the inside of vats and tanks used for other chemical processes. Large quantities of it are made into shot and bullets, the plates

of storage batteries, and **alloys**, such as type-metal, solder, pewter, fuse wire, etc. (cf. §§ 370, 374, and 515). Shot contains about 0.5% of arsenic.

513. Lead Compounds. — In its common salts — **plumbic** salts — lead is bivalent. These are made by treating **lead monoxide** (PbO) with acids. **Lead hydroxide**, $\text{Pb}(\text{OH})_2$, is both a base and a weak acid (*plumbous* acid).

Lead monoxide exists as a yellowish-red, crystalline mass (“**litharge**”), and also as a yellow powder (“**massicot**”). Litharge is made in large quantities in the separation of lead and silver (cf. § 462). Massicot may be made by heating lead nitrate or carbonate. A mixture of lead oxide and glycerine “sets” to a hard, compact mass, and is used as a glass cement. Lead oxide is also used in making glass (cf. § 394), glazes for pottery (§ 479), and for varnishes.

“**Red lead**,” or *minium* (Pb_3O_4) is made when litharge is oxidized by heating it in the air to 400°C . A mixture of red lead and linseed oil hardens rapidly, owing to the oxidation of the oil by the lead compound (cf. § 31); hence it is used to make tight joints in gas pipes, etc. Minium is also used to make a red paint for iron work.

Lead dioxide, PbO_2 . When red lead is treated with dilute nitric acid, lead dioxide remains as a brown powder. Both red lead and the dioxide react with hydrochloric acid to give *chlorine*.

Lead also forms a **suboxide**, Pb_2O , and a **trioxide**, Pb_2O_3 .

Lead nitrate, $\text{Pb}(\text{NO}_3)_2$, is made from litharge and nitric acid; **lead acetate**, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$, from litharge and acetic acid. Both are white, crystalline, and soluble. Lead acetate is called “sugar of lead.” **Lead sulphate** (PbSO_4) and **lead chromate** (PbCrO_4 ; cf. § 508) are insoluble in water. Lead

sulphate is somewhat soluble in concentrated sulphuric acid (*cf.* § 267).

Lead chloride, PbCl_2 , forms white crystals, difficultly soluble in cold water, but soluble in hot water. The **iodide**, PbI_2 , forms glistening, yellow crystals. It is less soluble than the chloride. **Lead tetrachloride**, PbCl_4 , is a yellow liquid obtained when lead dioxide is treated with very cold, concentrated hydrochloric acid. It is unstable, breaking down into lead chloride and chlorine. The corresponding MnCl_4 has never been made (*cf.* § 138).

Lead sulphide, PbS , is obtained as a black precipitate when a solution containing ionic lead (Pb^{++}) is treated with one containing ionic sulphur (S^{--}). The free elements also unite directly. Lead sulphide is oxidized to the sulphate when heated in the air. **Lead carbonate**, PbCO_3 , is precipitated from solutions of lead salts by ammonium carbonate or sodium bicarbonate solutions. The *normal* carbonates of sodium and potassium precipitate **basic** lead carbonate. **White lead** is a mixture of *basic lead carbonates*, the chief one being $\text{Pb(OH)}_2 \cdot 2 \text{PbCO}_3$. Several methods are used in making it; the oldest and best is the **Dutch process**. In this process gratings or "buckles" of lead are placed in earthenware pots containing a little vinegar, or dilute acetic acid. The pots are placed in layers, covered with planks, and buried in manure. The fermentation of the manure produces heat and carbon dioxide, and the lead "buckles" are converted, in three or four months, into the white basic carbonate. The reactions are essentially as follows:—

(1) $\text{Pb} + \text{O (from air)} + \text{HC}_2\text{H}_3\text{O}_2 \longrightarrow \text{Pb(OH)C}_2\text{H}_3\text{O}_2$ (basic acetate).

(2) $3 \text{Pb(OH)C}_2\text{H}_3\text{O}_2 + 2 \text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{Pb(OH)}_2 \cdot 2 \text{PbCO}_3 + 3 \text{HC}_2\text{H}_3\text{O}_2$.

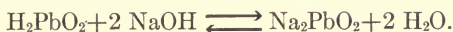
The **French process** consists in passing carbon dioxide into a

solution of basic lead acetate. The process is rapid, but the product is considered inferior to Dutch white lead.

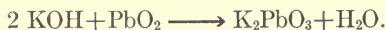
There is also an **electrolytic process**. This consists in passing a current, between lead electrodes, through a solution containing *sodium nitrate* (or chlorate) and *sodium bicarbonate*. The process is continuous, for sodium nitrate is regenerated. White lead is precipitated.

White lead is used for paints because of its opaqueness, or "covering" power. It is ground up with linseed oil. An objection to it is that it turns brown or black in the presence of hydrogen sulphide. "Zinc white" (ZnO) and "permanent white" (BaSO_4) are not blackened by H_2S , but they have not nearly the covering power of white lead.

Plumbites and Plumbates. Plumbites are formed when lead oxide or hydroxide "dissolves" in an excess of an alkali.



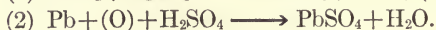
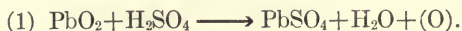
Plumbic acid forms *plumbates* derived from both its "ortho" form (H_4PbO_4) and its "meta" form (H_2PbO_3). Its anhydride is lead dioxide, PbO_2 . This "dissolves" in caustic potash solution, giving *potassium plumbate*.



Both red lead and lead trioxide give lead dioxide when treated with dilute nitric acid; hence they are considered to be *lead orthoplumbate* ($\text{Pb}_2^{\text{II}}.\text{PbO}_4$) and *metaplumbate* ($\text{Pb}^{\text{II}}.\text{PbO}_3$) respectively.

Storage Battery. — The common storage battery consists of two lead plates made in the form of "grids," and a bath of dilute sulphuric acid. The grids of one plate are filled with finely divided lead (made by reduction); while those of the other contain lead dioxide. The current owes its maintenance to the **oxidation** of the finely divided lead on the one plate to PbO , and the consequent **reduction** of the PbO_2 of the other plate

to PbO. Of course the acid present converts the PbO of both plates into PbSO₄. The equations for the **discharge** of the battery are: —



The battery is recharged by passing a current into it so as to reverse these changes, and to restore the plates to their original condition.

514. Occurrence and Metallurgy of Tin. — The source of tin is *cassiterite*, or tin-stone, SnO₂. This occurs in Alaska, Cornwall (England), Germany, Australia, and in Billiton and Banca, islands east of Sumatra.

Tin was known in very early times. The alloy **bronze**, consisting of copper and tin, was used before iron, and gave its name to the "Bronze Age." Although tin has been carried away from Cornwall since ancient times, the mines are still productive.

The metallurgy of tin consists, first, in *roasting* the ore, so as to oxidize and remove arsenic and sulphur. The tin oxide is then *reduced* with coal in a furnace, the metal being drawn off and cast into bars. These bars of impure tin are then slowly heated on a sloping hearth. The tin melts and runs down the hearth, leaving the unmelted impurities behind. **Banca tin** is the purest. That from Germany and England usually comes in *blocks*, whence the name **block tin**.

515. Properties and Uses. — Tin is a white metal, having a brilliant luster which does not tarnish in the air. It is soft and malleable, and melts at 233° C. The ordinary form changes into a gray, brittle form at low temperatures; hence tin organ-pipes, gutters, etc., are subject to "tin disease" in cold winter weather. The ordinary form is stable above 20° C. When a bar of tin is bent, it emits a grating noise ("cry of tin"), probably due to the friction between its crystals.

Tin *burns*, when sufficiently heated, giving *stannic oxide*, SnO_2 . With hydrochloric acid it gives *stannous chloride* (SnCl_2) and hydrogen. Hot, concentrated sulphuric acid produces *stannous sulphate* (SnSO_4) and sulphurous acid. Concentrated nitric acid oxidizes tin to an insoluble, white solid, *meta-stannic acid* (H_2SnO_3)₅. The dilute acid gives *stannous nitrate*, $\text{Sn}(\text{NO}_3)_2$, and *ammonium nitrate* (cf. § 227, end).

Uses of Tin. The chief use of tin is to coat iron, brass, and copper. **Tin-plate**, made by dipping iron into melted tin, is the material of "tin" cans and cooking utensils. Owing to its canning industries, the United States is the greatest **tin-consuming** country. **Pins** are made of brass wire (copper and zinc), and are coated with tin by dipping them into the solution of a tin salt. Copper utensils are also tinned to prevent corrosion.

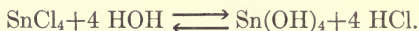
Tin is a constituent of many **alloys**, among them "*fusible alloys*" (cf. § 374), *bronze*, *bell-metal*, and *gun-metal* (q. v.). **Solder** usually contains 50% tin and 50% lead (cf. § 100, end). **Britannia metal** is about 90% tin, 8% antimony, and 2% copper.

Pewter is 75% tin and 25% lead. Tin is also used for pipes and as tin foil.

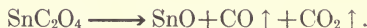
516. Tin Compounds. — Tin forms **stannous** compounds, in which the metal is *bivalent*, and **stannic** compounds, in which it is *quadrivalent*. It also forms **stannites** and **stannates**.

Stannous chloride, SnCl_2 , is formed from hydrochloric acid and an excess of tin. A little acid is added from time to time to react with the tin, and to keep the solution in reduced, i. e., *stannous*, form. Evaporation of the solution leaves colorless crystals ($\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$). Stannous chloride is easily oxidized to stannic chloride, and is, therefore, a **reducing agent**. It reduces *mercuric chloride*, first, to *mercurous* chloride, and then to *mercury* (cf. § 181). It reduces ferric to ferrous salts (cf. § 491). In the presence of acid, the air oxidizes it to stannic chloride. Stannous chloride is used as a mordant (cf. § 477).

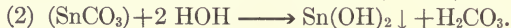
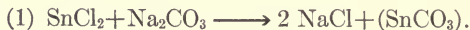
Stannic chloride, SnCl_4 , is made, in solution, by treating tin with aqua regia. The anhydrous substance is a colorless, fuming liquid, made by passing dry chlorine over heated tin. Its solution is hydrolyzed.



Stannous oxide (SnO) is a black powder made by heating *stannous oxalate*, or *hydroxide*, out of contact with air (cf. § 287).



Stannous hydroxide, $\text{Sn}(\text{OH})_2$ or $\text{H}_2\text{O} \cdot 2 \text{SnO}$, is formed as a white precipitate when a stannous salt is treated with sodium carbonate.



The hydroxide gives soluble **stannites** when treated with caustic alkalis. The stannites are reducing agents.

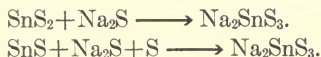
Stannic oxide, SnO_2 , is made by burning tin or *stannous oxide* (SnO), and by heating stannic acid. SnO_2 shows its acid character, and its analogy to CO_2 , SiO_2 , and PbO_2 , by reacting with molten alkalis to form *stannates*, e. g., Na_2SnO_3 .

Stannic acid, if it could be obtained as a definite compound, would be H_4SnO_4 or H_2SnO_3 . It loses water, giving its *anhydride*, SnO_2 . **Metastannic acid** is its insoluble **polymer**, $(\text{H}_2\text{SnO}_3)_5$ [cf. § 219]. When fused with alkalis, metastannic acid gives sodium stannate. This can be obtained as crystals, $\text{Na}_2\text{SnO}_3 \cdot 3 \text{H}_2\text{O}$.

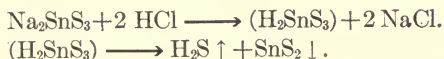
Stannous sulphide, SnS , is a *brown* powder, formed by heating tin with sulphur, or by passing hydrogen sulphide into a solution of a stannous salt.

Stannic sulphide, SnS_2 , is a *yellow* solid, made from hydrogen sulphide and a stannic salt, and used as a pigment ("mosaic gold"). When heated, it gives stannous sulphide and sulphur.

Sulphostannates are formed by the union of the tin sulphides with soluble sulphides, e. g., Na_2S . With SnS a **polysulphide** (cf. §§ 419 and 427) must be used.



Sulphostannates of the alkali metals are **soluble**; hence the tin sulphides, like those of *arsenic* (§ 365) and of *antimony* (§ 369) "dissolve" in alkali sulphides. **Gold sulphide** (Au_2S_3) and **platinum sulphide** (PtS_2) act in the same way. Sulphostannates react with strong acids, giving *sulphostannic acid*, H_2SnS_3 . This is unstable; the *metal sulphide* and *hydrogen sulphide* are formed (cf. § 365; also H_2CO_3 , § 282).



517. Platinum; Occurrence and Preparation.—Platinum is found **native** (*cf.* “Electromotive Series,” § 405 and Appendix x), but only small deposits are known. Some is found in Australia and California, but most of it comes from the Ural Mountains (Western Siberia).

Native platinum is usually mixed with five other rare metals, all belonging to the **eighth** periodic group. These are: palladium, ruthenium, rhodium, osmium, and iridium. About 75% of the ore is platinum.

The ore is treated with aqua regia, which reacts with the platinum and some iridium. The resulting *chlorplatinic acid*, H_2PtCl_6 (*cf.* § 519), is treated with ammonium chloride, producing a precipitate of *ammonium chlorplatinate* $(\text{NH}_4)_2\text{PtCl}_6$. When this is heated strongly, platinum results. The small quantity of iridium is not removed.

518. Properties and Uses.—Platinum is a grayish-white metal, of high luster, and of specific gravity 21.5. Air has no action upon it, and the temperature of the oxy-hydrogen flame is needed to melt it. Platinum does not react with the common acids, but is attacked by **aqua regia** and by *chlorine-* and *bromine-water*. **Fused alkalis** react with it, giving *platinates*, but alkali carbonates do not.

Finely divided forms of the element are known as **platinum black** and **platinum sponge**. Platinum black is made by *reducing* a platinum compound in solution, as when zinc is added to chlorplatinic acid; the spongy form, by heating $(\text{NH}_4)_2\text{PtCl}_6$. Both of these are active catalyzers (*cf.* § 260). Owing to its

power of condensing oxygen on its surface, and of occluding hydrogen (*cf.* § 53), platinum in finely-divided form causes instant union of the oxy-hydrogen mixture.

The resistance of platinum to most chemicals, and its high melting point, make it very useful in the laboratory. It is used as foil, crucibles, wire, etc. Large retorts of platinum are used in concentrating and distilling sulphuric acid (*cf.* § 263). Because it expands at the same rate as glass, platinum wire is melted into the glass of incandescent lamps to give connection with the carbon filament inside the lamp. Platinum vessels should never be used for heating substances that can set free phosphorus, silicon, antimony, lead, or, in general, any of the metals; neither should they be heated in smoky flames.

Chlorplatinic Acid. When platinum is treated with aqua regia, the platinum chloride (PtCl_4) formed unites with hydrochloric acid, giving chlorplatinic acid, H_2PtCl_6 . This is used for "toning" platinum photographs (*cf.* § 466). The solution of this substance gives with potassium salts and with ammonium salts precipitates of *potassium chlorplatinate*, K_2PtCl_6 , and of *ammonium chlorplatinate*, $(\text{NH}_4)_2\text{PtCl}_6$, respectively. The sodium salt is soluble. A solution of chlorplatinic acid thus serves as a test for potassium salts (K^+), even when sodium salts are present.

519. Exercises.

1. Write the equations for the following reactions: —

- (a) Lead acetate and zinc.
- (b) Lead, in presence of air, and acetic acid.
- (c) Lead, in presence of air, and **excess** of CO_2 .
- (d) Litharge and sand; red lead and hydrochloric acid.
- (e) "Solution" of lead sulphate in concentrated H_2SO_4 .
- (f) Lead chloride and potassium iodide solutions.
- (g) Lead nitrate and sodium bicarbonate solutions.
- (h) Red lead and dilute nitric acid.

- (i) Tin and concentrated, hot sulphuric acid.
 - (j) Tin and dilute nitric acid.
 - (k) Tin and concentrated nitric acid.
 - (l) Brass and stannous chloride.
 - (m) Mercuric chloride treated with a *little* of stannous chloride; with an excess.
 - (n) Acidified stannous chloride in contact with air.
 - (o) Auric sulphide (Au_2S_3) and ammonium sulphide.
 - (p) Platinum sulphide (PtS_2) and potassium sulphide.
 - (q) Platinum and carbon (hot).
 - (r) Effect of heating ammonium chloroplatinate.
2. How would you distinguish lead from tin? From zinc? From aluminum? From iron? From platinum?
3. Why are not "zinc-white" and "permanent-white" affected by hydrogen sulphide?
4. Give the chemical reasons for the objection to an alloy of tin and lead as the protective covering of iron cooking utensils. For the objection to galvanized iron.

CHAPTER XXXVIII.

SOME CARBON COMPOUNDS.

520. Organic Chemistry. — It was formerly believed that the complex substances produced by animals and plants, such as sugar, starch, uric acid, etc., could not be made in the chemical laboratory; hence there arose a distinction between “*organic*” and “*inorganic*” compounds. Organic compounds, it was thought, needed “vital energy” for their formation, while inorganic substances could be made without the intervention of living things. However, the preparation of *urea*, $\text{CO}(\text{NH}_2)_2$, an animal product, by Wöhler in 1828 and the many organic syntheses made since that time have destroyed the force of this distinction. At the present time the term “Organic Chemistry” is practically equivalent to “Chemistry of the Carbon Compounds.”

The carbon compounds exceed in number those of all the other elements together, yet each substance is composed of relatively few elements. Many compounds contain only carbon and hydrogen; a much larger number, carbon, hydrogen, and oxygen. Many important organic substances contain carbon, hydrogen, and nitrogen, while others have oxygen in addition. Phosphorus, sulphur, and the halogens are also present in many organic compounds.

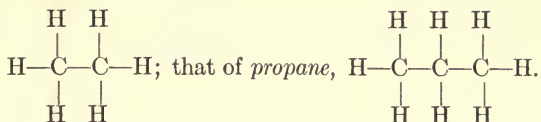
The compounds described in this chapter are classified as (1) hydrocarbons, (2) alcohols, (3) ethers, (4) aldehydes, (5) acids, (6) organic salts, or esters, (7) amines and alkaloids, (8) carbohydrates, and (9) phenol derivatives.

521. Hydrocarbons of Marsh Gas Series. — Substances composed of only hydrogen and carbon are called *hydrocarbons*. Several have already been mentioned in §§ 291 to 297. *Methane* (§ 291) is the first member of a large series — the **marsh gas**, or **paraffin series** — in which the formula of each member differs from that of the next member by CH_2 . Such a series is said to be *homologous*.

The names and formulas of some members of the paraffin series are given in the first column of the accompanying table. The formulas show that the number of hydrogen atoms in the molecule of each of these hydrocarbons is two more than twice the number of carbon atoms; hence the series may be represented by the *general formula* $\text{C}_n\text{H}_{2n+2}$.

To explain the fact that so large a number of marsh gas hydrocarbons exists, chemists have assumed that carbon is *tetravalent* in these compounds (cf. §§ 133 and 135), and that the carbon atoms are *united in chains*.

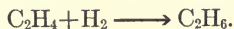
The constitutional formula for marsh gas has been given (cf. § 218). That of *ethane* is —



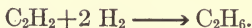
MARSH GAS SERIES.	ETHYLENE SERIES.	ACETYLENE SERIES.	POLYMETHYLENE SERIES.	BENZENE SERIES.
Methane, CH ₄ .				Benzene, C ₆ H ₆ .
Ethane, C ₂ H ₆ .	Ethylene, C ₂ H ₄ .	Acetylene, C ₂ H ₂ .		Toluene, C ₇ H ₈ .
Propane, C ₃ H ₈ .	Propylene, C ₃ H ₆ .	Allylene, C ₃ H ₄ .	Trimethylene, (CH ₂) ₃ .	Xylene, C ₈ H ₁₀ .
Butane, C ₄ H ₁₀ .	Butylene, C ₄ H ₈ .	Crotonylene, C ₄ H ₆ .	Tetramethylene, (CH ₂) ₄ .	Mesitylene, C ₉ H ₁₂ .
Pentane, C ₅ H ₁₂ .	Amylene, C ₅ H ₁₀ .		Pentamethylene, (CH ₂) ₅ .	
Hexane, C ₆ H ₁₄ .	Hexylene, C ₆ H ₁₂ .		Hexamethylene, (CH ₂) ₆ .	

The highest known member of the marsh gas series has the formula C₆₀H₁₂₂. The members from butane to *pentadecane*, C₁₅H₃₂, are liquids at ordinary temperatures; those of greater molecular weight, solids.

522. Ethylene and Acetylene Series. — As we learned in § 294, ethylene can unite with chlorine and bromine directly; it can also take up hydrogen, producing *ethane*.

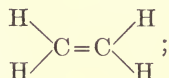


The molecule of acetylene can take up **twice** as much of these substances as the molecule of ethylene.



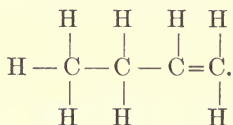
Because of their ability to unite with hydrogen, etc., to form marsh gas derivatives, both ethylene and acetylene are said to be *unsaturated*, to distinguish them from methane and its homologues, which are *saturated*. We explain the unsaturation existing in these compounds by assuming that all the valences of the carbon atoms are not used.

Ethylene is represented by the constitutional formula,—



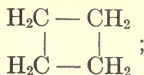
acetylene by $\text{H} - \text{C} \equiv \text{C} - \text{H}$.

The homologues of ethylene and acetylene contain chains of carbon atoms with both saturated and unsaturated groups. Thus, the constitutional formula of *butylene* (see table) is —



523. Closed and Open Chains. — The chains of carbon atoms in substances already described are called “open” chains to distinguish them from groups of atoms in *rings*, which are called “closed” chains. The *polymethylene* and *benzene* derivatives named in the table contain closed chains.

Thus, the constitutional formula of *tetramethylene* is —



that of *benzene*, $\text{HC} \begin{array}{l} \diagup \text{CH} = \text{CH} \diagdown \\ \diagdown \text{CH} - \text{CH} \diagup \end{array} \text{CH}.$

In *thiophene*, $\begin{array}{c} \text{HC} = \text{CH} \\ | \quad \quad \diagdown \\ \text{HC} = \text{CH} \diagup \end{array} \text{S},$

a sulphur atom forms part of the ring.

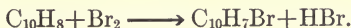
524. Benzene Hydrocarbons. — In § 297 it was stated that benzene is obtained from coal tar. When the coal tar is distilled, it yields several *fractions* the lower of which contain benzene and toluene, while higher-boiling portions consist of *xylene*, *naphthalene*, *anthracene*, etc.

Benzene is a colorless, aromatic liquid which boils at 80° C. and does not mix with water. It burns with a smoky flame. Solid benzene melts at 6° C. Benzene is used as a solvent and as a source of benzene derivatives, chiefly *nitrobenzene*, $\text{C}_6\text{H}_5\text{NO}_2$ (*cf.* § 232).

Nitrobenzene is a yellow liquid boiling at 205° C. It has the odor and taste of bitter almonds.

Toluene is *methylbenzene*, $\text{C}_6\text{H}_5\text{CH}_3$. It boils at 110°.

Napthalene, C_{10}H_8 , is a white solid melting at 79° and boiling at 218°. It is used for “moth balls” and in the preparation of dyes. It reacts with bromine according to the equation,



This is a good laboratory method for generating hydrogen bromide (*cf.* § 321).

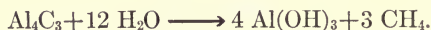
Anthracene, $C_{10}H_{14}$, is a white solid melting at 213° and boiling about 350° . It is used as a source of the valuable red dye *alizarin*, which occurs naturally in madder root.

Turpentine is a resinous substance obtained from incisions in the bark of pines. By distillation it yields *oil of turpentine*, which consists largely of a hydrocarbon, $C_{10}H_{16}$ (*cf.* § 121). The residue is *rosin*.

525. Petroleum. — Petroleum is a thick, oily liquid obtained from the earth in many places. It consists essentially of a mixture of hydrocarbons, with larger or smaller amounts of nitrogen and sulphur compounds. The largest deposits are in the United States and Russia, but it occurs also in Japan, India, and Austria. In 1911 the United States produced about 220,000,000 barrels of the crude oil, valued at about \$135,000,000.

It is uncertain how petroleum was produced, whether by the decomposition of animal or plant remains or by the action of water, under great pressure, upon *carbides*, particularly the carbide of iron.

Aluminum carbide and water react according to the equation,



Refining. — Some crude petroleum is used as a fuel and to enrich water-gas (*cf.* § 298), but most of it is *refined*. The petroleum is carried from the wells to the refineries through long systems of pipes. In the refining process it is shaken successively with

sulphuric acid, caustic soda or potash solution, and water. It is then distilled, and the distillates which pass over between certain degrees of temperature are collected by themselves. Thus many *fractions* are obtained. The lowest fraction boils about $18^{\circ}\text{C}.$, and is called *rhigolene*. This is used as a refrigerating agent. Between 18° and 250° *gasoline*, *benzine* (not benzene), *petroleum ether*, *ligroin*, *kerosene*, etc., are collected. They are used as fuels and solvents. The higher-boiling products are converted into mineral lubricating oils, *vaseline*, and *paraffin* (white wax). Coke remains in the retort. Over two hundred commercial products are now made from petroleum.

526. Natural Gas. — In many places a combustible gas has collected in large, underground “pockets,” and is released by drilling wells. The gas consists largely of *methane* (cf. § 292), and is carried to consumers in pipes, as in the case of illuminating gas. The value of the natural gas produced in the United States in 1910 was nearly \$71,000,000.

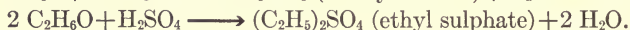
527. Alcohols. — The alcohols form a large and important class of organic substances, and include several homologous series. The first member of one of these series is *methyl alcohol*, CH_4O , and its second member is *ethyl alcohol*, $\text{C}_2\text{H}_6\text{O}$. Methyl alcohol is called “wood spirit,” because it is obtained

in the dry distillation of wood (*cf.* § 275). It boils at 66° C. Ethyl alcohol boils at 78° C. Both are colorless liquids.

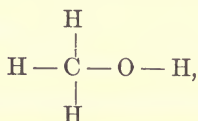
The alcohols react with metals much as water does (*cf.* § 74). Thus, ethyl alcohol and sodium produce *sodium ethylate* and hydrogen.



With acids the alcohols react like hydroxides of the metals, giving *salts* and water.



These equations are like those for the reactions of potassium and sodium hydroxides with the acids (*cf.* §§ 160 and 226), consequently the alcohols are looked upon as *hydroxides*. The formula of methyl alcohol is, therefore, written CH_3OH , or



and that of ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$ (*cf.* § 220). The group CH_3 is the **radical** “methyl” (*cf.* § 210), and methyl alcohol is *methyl hydroxide*. The radical C_2H_5 is called “ethyl.”

Some properties of the first five alcohols of the series are given in the table.

ALCOHOL.	FORMULA.	BOILING POINT.	SPECIFIC GRAVITY AT 20° C.
Methyl.	CH_3OH	66°	0.796
Ethyl.	$\text{C}_2\text{H}_5\text{OH}$	78°	0.789
Propyl.	$\text{C}_3\text{H}_7\text{OH}$	97°	0.804
Butyl.	$\text{C}_4\text{H}_9\text{OH}$	117°	0.810
Amyl.	$\text{C}_5\text{H}_{11}\text{OH}$	138°	0.817

Both ethyl and methyl alcohols burn with colorless, hot flames. They mix with water, dissolve fats, oils, and gums, and are used in the manufacture of dyestuffs and varnishes. Ethyl alcohol is used as a solvent in the preparation of essences, extracts, perfumes, and medicines. It is also used to preserve anatomical specimens.

Ethyl alcohol solidifies at -112.3°C . and is used for thermometers reading below the freezing point of mercury (-39.5°).

528. Preparation of Ethyl Alcohol. — As already stated in § 280, *a*, alcohol is formed by the fermentation of sugar. Before cane sugar can be fermented it must be changed to grape sugar (*cf.* § 543). The agent of alcoholic fermentation is *zymase*, a ferment present in yeast.

To prepare alcohol on a large scale starchy substances, such as potatoes, grains, rice, etc., are

allowed to sprout and develop far enough to change much of their starch into sugar. This is then fermented by adding yeast. Besides alcohol and carbon dioxide, small amounts of *glycerine* and of *propyl*, *butyl*, and *amyl* alcohols are formed. The mixture of these alcohols is called "**fusel oil**."

The ethyl alcohol is separated from most of the water and fusel oil by distillation, but the product ("95 per cent" alcohol) still contains from *four* to *ten* per cent of water. This may be almost entirely removed by distilling the commercial alcohol with lime. The distillate is called *absolute* alcohol.

529. Liquors.

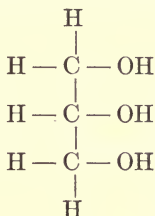
Wines are prepared by allowing the ferments present in the air (*cf.* § 190) to act upon the juice of grapes. Beers are produced in a similar way from hops and malt (sprouted barley). When the fermented solution contains from 10 to 14% alcohol, action of the yeast ferment stops entirely. Liquors containing a larger proportion of alcohol have been distilled, or the alcohol has been added directly. The colors and flavors of liquors are due to substances present before fermentation or produced while the liquor stands in casks, or to foreign substances added.

Beer has ordinarily from 3 to 7% of alcohol; wine, 5 to 20%; and whiskey, gin, and rum, above 40%. In dilute form, alcohol acts as an intoxicant; undiluted, it is a poison.

530. Glycerine. — $C_3H_8O_3$. — Glycerine is a sweet, colorless, viscous liquid produced by the hydrolysis of fats (*cf.* §§ 413 and 540). It is soluble in alcohol and in water and absorbs moisture from the air. It is

used in making nitroglycerine (*cf.* § 232), soaps, cosmetics, and inks; also as a food preservative and a lubricator. It boils at 290°C .

Glycerine is a complex alcohol. Its constitutional formula is



531. Ethers. — If R represents an organic *radical*, ROH is the *general formula* of an alcohol (*cf.* table, § 527). We represent an *ether* by $\text{R} - \text{O} - \text{R}$, or R_2O . If the R of R_2O is CH_3 , we have the formula of *methyl ether*; if C_2H_5 , that of *ethyl ether*. For methyl ether see § 220.

Ethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$, is also called “sulphuric ether.” It is a colorless, volatile liquid having a sweet odor. It boils at 35°C ., is *very inflammable*, and is an excellent solvent for organic compounds. Ether is used in surgery as an anesthetic. For its solubility in water see § 82.

Preparation. — Ether is made in the laboratory (Fig. 91) by heating a mixture of ethyl alcohol and sulphuric acid to 140° (*not higher*) and keeping it at this temperature while adding alcohol in a slow stream through a separatory funnel.

The mixture of alcohol and ether which distills off is redistilled carefully. The rubber tube attached to the receiver (see

Fig. 91) carries any uncondensed vapor of ether away from flames. The equations are:

1. $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{SO}_4 \longrightarrow \text{C}_2\text{H}_5\text{HSO}_4 + \text{H}_2\text{O}.$
2. $\text{C}_2\text{H}_5\text{OH} + \text{C}_2\text{H}_5\text{HSO}_4 \longrightarrow (\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{SO}_4.$

$\text{C}_2\text{H}_5\text{HSO}_4$ is *ethyl hydrogen sulphate* (cf. § 164).

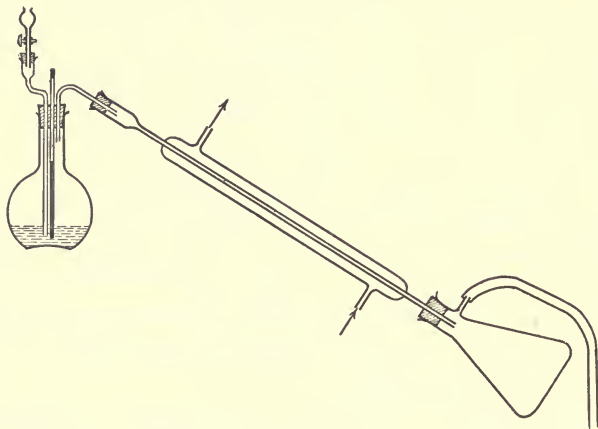
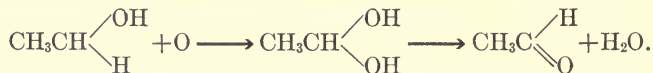


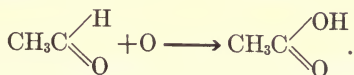
FIG. 91.

532. Aldehydes. — The oxidation of ethyl alcohol by a mixture of potassium dichromate and dilute sulphuric acid produces acetaldehyde, CH_3CHO ; called, also, simply *aldehyde* (cf. § 509).



Aldehyde is a colorless liquid boiling at $21^\circ \text{C}.$ and very soluble in water. It is reduced by nascent

hydrogen (cf. § 123), giving *ethyl alcohol*. With oxidizing agents it gives *acetic acid*.



Aldehyde is used to reduce silver solutions containing ammonia, as in the "silvering" of mirrors (cf. § 464). The name "aldehyde" is derived from

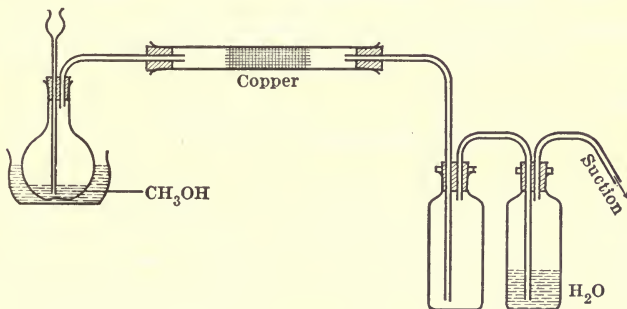


FIG. 92.

al(cohol) de hyd(ro)genatus), i. e., "alcohol deprived of hydrogen."

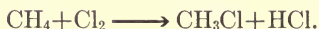
Formaldehyde, $\text{H}_2\text{C}=\text{O}$, is made by the oxidation of methyl alcohol. The laboratory method (Fig. 92) is to draw air through *warm* methyl alcohol and then to draw the mixture of air and alcohol vapor over heated copper.



Formaldehyde is a colorless, irritating gas, very soluble in water. It is used as a disinfectant and preservative. *Formalin* is a 40% solution of formaldehyde.

Benzaldehyde, C_6H_5CHO (see table, § 538), is the oil of bitter almonds found in almonds and cherry kernels. It has a pleasant odor, boils at 179° , and is used as a flavor.

533. Halogen Derivatives. — When marsh gas is treated with chlorine in diffused light, the products are *methyl chloride* (chlormethane) and hydrochloric acid.



Under proper conditions the reaction may go further, giving *dichlormethane* (CH_2Cl_2), *trichlormethane* ($CHCl_3$), and even *tetrachlormethane* (CCl_4). Methyl chloride is gaseous at ordinary temperatures; the others are colorless liquids. Trichlormethane is **chloroform**, the anesthetic (*cf.* 389). It boils at $63^\circ C$.

Chloroform is generally prepared by the action of bleaching powder upon alcohol or *acetone*, $(CH_3)_2CO$. It may also be made by the action of alkalis upon *chloral* (trichloroacetaldehyde), CCl_3CHO .

Chloral is made by the action of chlorine upon alcohol; it is a liquid with a disagreeable odor. Like other aldehydes it combines with water, giving a *hydrate*. Chloral hydrate is often used by physicians to produce sleep.

Iodoform, CHI_3 , is analogous to chloroform. It is a yellow solid, melting at 119° . It is used as a surgical dressing.

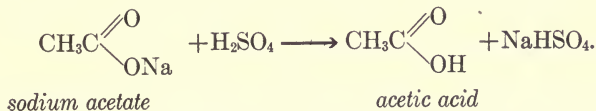
534. Organic Acids. — The organic acids are oxidation products of the corresponding aldehydes.

While the general formula of aldehydes is $\text{R}-\text{C}\begin{smallmatrix} \text{H} \\ \text{O} \end{smallmatrix}$,

that of acids is $\text{R}-\text{C}\begin{smallmatrix} \text{OH} \\ \text{O} \end{smallmatrix}$. The acids may be

mono-, di-, tri-basic, etc. The hydrogen of the CO.OH group is the *ionic* hydrogen (*cf.* § 176).

535. Acetic Acid. — Acetic acid (*cf.* §§ 158 and 275) is formed by the dry distillation of wood. The crude product (*pyroligneous acid*) is neutralized with lime or caustic soda. The resulting *acetate* is then purified and treated with concentrated sulphuric acid. The reaction is like that between chlorides, etc., and sulphuric acid (*cf.* § 225).



If the acetate used is *anhydrous* the acid is obtained as a sharp-smelling liquid which solidifies to

colorless crystals melting at about 17° C. (**glacial acetic acid**). It boils at 118° C. and mixes readily with water.

Sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2 + 3 \text{H}_2\text{O}$, is a white solid used in making dyes. It loses its crystal water when heated.

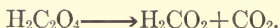
Lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3 \text{H}_2\text{O}$ (cf. § 513), is used in making *lead chromate* (chrome yellow) and in dyeing (§ 508).

Impure *iron* and *aluminum* acetates are used as mordants in dyeing and in the printing of calico.

Verdigris, used for a blue paint, is basic copper acetate.

Paris green, an arseno-acetate, was mentioned in § 363.

536. Formic Acid, H_2CO_2 . — Formic acid is found in stinging nettles and the bodies of red ants. It is prepared by heating *oxalic acid* with glycerine.



The anhydrous acid melts at 4° C. and boils at 100°. It produces blisters on the skin.

537. Vinegar. — As was stated in §§ 280 and 528, a ferment in yeast decomposes sugar, giving alcohol and carbon dioxide. If the dilute, impure alcohol (wine or cider) is allowed to stand in the air, a new fermenting agent ("mother of vinegar") oxidizes it to aldehyde and acetic acid. The dilute, impure acetic acid that results is *vinegar*.

On a large scale, vinegar is made in casks or vats filled with shavings and perforated so that air has free access. The shavings are "inoculated" by means of strong vinegar, and the dilute alcohol is allowed to trickle over them.

538. Other Acids. — Acetic and formic acids are the first members of an homologous series. The relation between some of these acids and the corresponding *hydrocarbons*, *alcohols*, and *aldehydes* is shown in the table. All except the last two are derived from marsh gas hydrocarbons.

HYDRO-CARBON.	ALCOHOL.	ALDEHYDE.	ACID. FORMULA. NAME.
CH ₄	H.CH ₂ OH	H.CHO	H.COOH Formic.
C ₂ H ₆	CH ₃ CH ₂ OH	CH ₃ CHO	CH ₃ COOH Acetic.
C ₃ H ₈	C ₂ H ₅ CH ₂ OH	C ₂ H ₅ CHO	C ₂ H ₅ COOH Propionic.
C ₄ H ₁₀	C ₃ H ₇ CH ₂ OH	C ₃ H ₇ CHO	C ₃ H ₇ COOH Butyric.
C ₁₅ H ₃₄	C ₁₅ H ₃₁ CH ₂ OH	C ₁₅ H ₃₁ CHO	C ₁₅ H ₃₁ COOH Palmitic.
C ₁₈ H ₃₈	C ₁₇ H ₃₅ CH ₂ OH	C ₁₇ H ₃₅ CHO	C ₁₇ H ₃₅ COOH Stearic.
C ₁₈ H ₃₆			C ₁₇ H ₃₃ COOH Oleic.
C ₇ H ₈	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CHO	C ₆ H ₅ COOH Benzoic.

Butyric acid is present in butter as the glycerine ester (*cf.* § 540) and is set free when the butter becomes rancid.

Benzoic acid is a white solid melting at 121° C. and subliming when heated.

Oxalic acid forms white, soluble crystals having the formula H₂C₂O₄. 2 H₂O. It acts as a reducing agent (*cf.* § 503). It is used in some of the processes of dyeing and photography, and to remove ink spots and rust from fabrics.

Lactic acid, HC₃H₅O₃, is produced by the fermentation of milk sugar (*cf.* § 543) and is, therefore, found in sour milk. It is present also in pickles and in the gastric juice. It is a thick, colorless liquid which decomposes when heated.

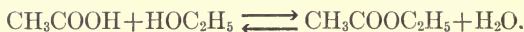
Tartaric acid, H₂C₄H₄O₆ (*cf.* § 158), forms large crystals. Its potassium hydrogen salt ("cream of tartar"; *cf.* § 280, b)

is obtained from the walls of wine casks as a dark solid called "tartar" or "argol." From this the acid is prepared. For "tartar emetic" see § 369.

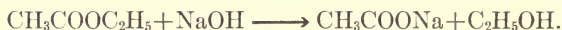
Malic acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_5$, occurs in fruits. It forms deliquescent crystals melting at 100° .

Citric acid, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 + \text{H}_2\text{O}$, forms crystals melting at 100° . It occurs in lemons, oranges, and other acid fruits. *Magnesium citrate* is a medicine.

539. Esters. — Alcohols react with acids (*cf.* § 527) producing water and *organic salts*, or **esters**. Thus acetic acid and alcohol produce ethyl acetate and water.



The reaction is, however, **reversible**: water saponifies the ester (*cf.* § 413). To make the formation of the ester complete we remove the water from the "sphere of action" by means of concentrated sulphuric acid. Alkalies and dilute acids saponify the esters more rapidly than water. For ethyl acetate and sodium hydroxide the equation is:



Many esters present in fruits and flowers give to them a characteristic odor and taste. Artificial esters are often used instead of the natural flavors in the preparation of drinks, extracts, and perfumes. Thus *ethyl butyrate* has the odor and taste of pineapples; *amyl acetate*, that of bananas; *amyl valerate*, that of apples.

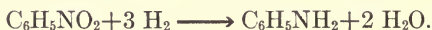
540. Fats and Oils; Soaps. — The most important esters are the natural fats and oils, which consist essentially of the glycerine esters of *stearic*, *oleic*, and *palmitic* acids. These esters are called *stearin*, *olein*, and *palmitin*, respectively. The relative amount of olein present in the fats largely determines their fluidity, since olein is liquid at ordinary temperatures. The other two esters are solids. *Tallow* and *beef-suet* are largely stearin; *palm oil* is largely palmitin; *lard* and *olive oil* contain much olein; while *butter* is a mixture of several fats, — esters of palmitic, stearic, oleic, butyric, caproic, and capric acids. The last two have the formulas $C_5H_{11}COOH$ and $C_9H_{19}COOH$, respectively.

Soap. In making soap (*cf.* § 413) the alkali and the fat are heated in large kettles until the fat is saponified. The soap remains in solution until salt is added, which makes it rise to the top of the mixture. The salty solution is worked up for *glycerine*, while the soap is washed, perfumed, and colored, or “filled” with borax, sand, etc. It is then cut into bars and dried.

Hard soaps consist of the sodium salts, and soft soaps of the potassium salts of the organic acids. Palm oil, cocoanut oil, tallow and lard produce *white* soaps. In the *yellow* varieties these fats are mixed with rosin, cotton-seed oil, bone grease, etc. Olive oil is used in making “Castile” soap.

541. Amines. — Amines are composed of carbon, hydrogen, and nitrogen. They may be looked upon as *ammonia* with its hydrogen replaced by organic radicals (*cf.* § 527). *Methylamine* (CH_3NH_2) and

ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$) are gases much like ammonia. They are very soluble in water and unite with acids, forming salts. The most important amine is **aniline** (phenylamine), $\text{C}_6\text{H}_5\text{NH}_2$. This is a colorless liquid made by reducing nitrobenzene.



The nitrobenzene is reduced by adding to it tin (or iron) and hydrochloric acid. The resulting *aniline hydrochloride*, $\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{HCl}$, is a white solid like ammonium chloride (*cf.* § 210). It is decomposed by caustic soda, liberating aniline.

Aniline is used in making aniline dyes and many other organic substances.

542. Alkaloids. — Alkaloids are nitrogenous substances occurring in plants and often used in medicine because of their physiological effect. Chemically they resemble ammonia: they unite with acids to form salts, and their aqueous solutions are alkaline.

Quinine, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$, is found in the bark of cinchona trees, and is used to reduce fevers.

Morphine, $\text{C}_{17}\text{H}_{19}\text{NO}_3$, which occurs with other alkaloids in *opium*, is used to deaden pain. Opium is made by evaporating the sap of unripe poppies. *Paregoric* and *laudanum* are prepared from it.

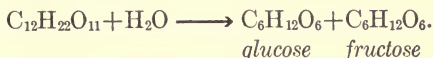
Strychnine ($\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$) and *brucine* ($\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4$) occur in *nux vomica*.

Cocaine is found in cocoa leaves. Its salt, $\text{C}_{17}\text{H}_{21}\text{NO}_4 \cdot \text{HCl}$, is used by dentists and surgeons as a local anesthetic.

Theïne (or *caffeine*), $C_8H_{10}N_4O_2 + H_2O$, is the active constituent of tea and coffee.

Nicotine, $C_{10}H_{14}N_2$, occurs in tobacco as the *malate*.

543. Sugars. — Sugars, starch, and cellulose are the most important substances of the class of compounds known as *carbohydrates*. The most common sugar is *cane sugar*, which is made from sugar cane and from beets. Its formula is $C_{12}H_{22}O_{11}$. Isomeric with it (*cf.* § 220) are *maltose* (malt sugar) and *lactose* (sugar of milk). When cane sugar is exposed to certain ferments, or heated with dilute acids, it is *hydrolyzed* according to the equation:



Maltose decomposes according to a similar equation, but only glucose is formed. Lactose gives glucose and *galactose*. All sugars contain (OH) groups, like alcohols (*cf.* §§ 527 and 530).

Milk sugar is not so sweet as cane sugar. It forms hard, white crystals, and is used for prepared foods and homeopathic pellets. The lactic acid ferment decomposes it (*cf.* § 538).

Cane sugar melts at about 160° C. At about 200° it forms a brown substance called *caramel*, which is used as a coloring for foods and liquors.

544. Manufacture of Cane Sugar. — Cane sugar, or *sucrose*, is prepared from the cane by crushing it

and boiling the juice with lime. The lime clarifies the juice. After filtration the sugar solution is evaporated until a cooled sample begins to crystallize. The evaporation is then continued in "vacuum pans," so that the water distills off at a temperature below that at which it would boil under atmospheric pressure (*cf.* § 340). The crystals of sugar are separated from the liquid (molasses) by rotating the mixture in funnel shaped sieves through which only the molasses can escape. *Raw* or *brown sugar* is thus obtained. The preparation of sugar from beets takes place in a similar way.

The *second* operation is the **refining** of raw sugar. In this process the raw sugar is dissolved in hot water, the solution is stirred by blowing air through it, and coagulating substances are added to collect the impurities. Animal charcoal is used to make the solution colorless (*cf.* § 275). The resulting syrup is then concentrated in vacuum pans and left in tanks until it crystallizes. Finally the crystals of sugar are separated from the adhering syrup in centrifugal apparatus and dried carefully for the market.

545. Glucose and Fructose. — *Glucose*, $C_6H_{12}O_6$, — also called dextrose and grape sugar, — is a white, crystalline solid less sweet than cane sugar. It melts at about $150^\circ C$. Glucose is found in grapes, and, therefore, in raisins. It occurs in the seeds,

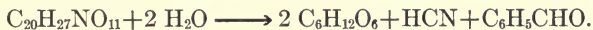
roots, leaves, and blossoms of plants, and is formed by the hydrolysis of sucrose, maltose, and lactose. Glucose reduces alkaline copper solution (Fehling's solution) giving *cuprous oxide* (cf. § 459).

Fructose (levulose or fruit sugar) is isomeric with glucose. It is a white solid, melting at 107° – 109° , and is almost as sweet as sucrose. Both glucose and fructose are fermentable.

Commercial glucose is made by heating starch with dilute sulphuric acid. This hydrolyzes the starch, giving several intermediate products, and finally glucose. The part that crystallizes out is called "grape sugar," while the colorless syrup is called "glucose" or "mixing syrup." "Glucose" is used in the preparation of jellies, candy, and syrups.

546. Glucosides. — While in cane sugar and milk sugar glucose is combined with fructose and galactose, respectively, in many other natural compounds it is combined with benzene derivatives. These are called *glucosides*. Amygdalin, the tannins, and indican are examples.

Amygdalin, $C_{20}H_{27}NO_{11}$, is found in bitter almonds and in the kernels of many fruits, such as peaches, cherries, and plums. The ferment *emulsin* and dilute acids decompose it into glucose, prussic acid, and benzaldehyde.



Tannins are found in the bark and leaves of many plants. The chief sources are hemlock and oak bark, but they occur

also in tea, sumach, gall nuts, etc. Not all of the tannins are glucosides.

The tannins are characterized by their ability to convert fresh skin into leather and by their forming black, green, or blue solutions or precipitates with iron salts. They are therefore used extensively in tanning and in making inks. They are also used as mordants in dyeing (*cf.* § 477).

The most important acids found in the tannins are *gallic acid* ($C_7H_6O_5$) and *tannic acid* (tannin), $C_{14}H_{10}O_9$.

Indican, $C_{26}H_{31}NO_{17}$, occurs in certain plants. When fermented, or when boiled with dilute acids, it breaks down into a sugar and **indigo blue**, the well known dyestuff. Indigo has the formula $C_{16}H_{10}N_2O_2$. It is now prepared synthetically in large quantities.

547. Starch. — Starch is found in grains, potatoes, and fruits. It is made from maize and potatoes by reducing them to powdered form, adding water, and separating the starch, which is practically insoluble, from the gluten, oil, and cellulose with which it is mixed.

Starch consists of small grains of varied appearance. Hot water causes the grains to swell and burst. The resulting **starch paste**, suspended in water, is called "starch solution." Starch is used in foods, in making cloth, paper, and glucose, and for "starching" clothes. The formula of starch is $(C_6H_{10}O_5)_n + H_2O$. The value of n is not known.

Dextrin is formed from starch by the action of dilute acids. The sticky solution (impure dextrin) is used for mucilage.

Bread is made from flour by the fermenting action of yeast. Wheat flour consists largely of starch (about 70%) with about 15% each of water and gluten, besides small amounts of salts and dextrin. When flour, water (or milk), and yeast are mixed into a dough and set in a warm place, the yeast changes sugar (present as such, or produced from the starch) into alcohol and carbon dioxide, and the bread "rises." In baking, the yeast is killed; water, carbon dioxide, and alcohol escape, and the starch on the outside of the bread is partly changed to dextrin, forming the crust.

548. Cellulose ($C_6H_{10}O_5$)_x. — Cellulose is the basis of vegetable tissue, since it forms the walls of plant cells. Cotton, linen, and paper are almost wholly cellulose. Swedish filter paper is a purified form. Cellulose is an amorphous, white substance insoluble in most solvents. When treated with concentrated sulphuric acid and then with water it breaks down into glucose. Like alcohols, cellulose reacts with acids to form *esters*. The nitric acid esters were mentioned in § 232. *Collodion* is nitrocellulose dissolved in alcohol and ether. When the solvent evaporates it leaves a thin film of nitrocellulose. Collodion can thus be used to protect wounds and to attach silver salts to photographic plates (*cf.* § 466).

Paper is made from rags, wood, or straw. The process consists of several stages:

1. Reducing the raw material to pulp and drying and pressing the pulp.
2. Mixing the pulp with clay or gypsum ("filling") to give the paper a close texture.

3. "Sizing" pulp that is to be converted into printing or writing paper, so that the ink will not spread. Gelatin, rosin, or alum is used for this.

4. Polishing the paper by passing it between rollers.

The conversion of wood into pulp is accomplished by first reducing it to chips and then heating the chips, under pressure, with sodium hydroxide or calcium acid sulphite ("bisulphite"; cf. § 259). Newspaper and wrapping paper are generally unsized; blotting and tissue papers are neither sized nor filled.

549. Phenol and its Derivatives. — Phenol, or *hydroxybenzene*, C_6H_5OH , is found in coal tar (cf. § 297). It is a white, crystalline, low-melting solid, which burns the skin and is poisonous. Its aqueous solution is used as a disinfectant. Phenol reacts with alkalis to give salts; it is sometimes called *carbolic acid*.

Salicylic Acid. When the sodium salt of phenol is treated with carbon dioxide at 120° , under pressure, the two unite to give *sodium salicylate*, $C_6H_4OH.COONa$. This is used in medicine. Salicylic acid is a white solid melting at 156° and used as a preservative. Its *methyl ester*, $C_6H_4OHC(=O)OCH_3$, is present in oil of wintergreen.

Picric Acid, or trinitrophenol, $C_6H_2(NO_2)_3OH$, is made from phenol and fuming nitric acid. It is a yellow, soluble solid used as a dye. Some of the picrates are used in making explosives.

Hydroquinone, $C_6H_4(OH)_2$, and **pyrogalllic acid**, $C_6H_3(OH)_3$, are di- and tri-hydroxybenzene, respec-

tively. They are soluble, white solids. Both are reducing agents and are used as developers in photography (*cf.* § 466). Pyrogalllic acid (also called *pyrogallol*) is used to absorb uncombined oxygen in gas analysis.

48 M M

1000 - 2 000

APPENDIX.

THE METRIC SYSTEM.

1. **Length.** The unit of length is the **meter** (39.37 in.).

10 millimeters (mm.)	= 1 centimeter (cm.).
10 centimeters	= 1 decimeter (dm.).
10 decimeters	= 1 meter (m.).
1,000 meters	= 1 kilometer (km.).

Note that the prefix "milli-" means 0.001, as *mill* = 0.001 dollar; "centi-" means 0.01, as *cent* = 0.01 dollar; "deci-" means 0.1, as *dime* = 0.1 dollar. "Kilo-" means 1,000.

2. **Square Measure, or Area.**

100 square millimeters (sq. mm.)	= 1 sq. centimeter (sq. cm.)
100 square centimeters	= 1 sq. decimeter (sq. dm.).
100 square decimeters	= 1 sq. meter (sq. m.).

3. **Cubic Measure, or Volume.** The unit of volume is the **liter**, which is 1 cu. dm., or 1,000 c.c.

1,000 cubic millimeters (cu. mm.)	= 1 cubic centimeter (c.c.).
1,000 cubic centimeters	= 1 cubic decimeter (cu. dm.).
1 cubic decimeter	= 1 liter (l.).
10 liters	= 1 dekaliter (dl.).
10 dekaliters	= 1 hectoliter (hl.).
10 hectoliters	= 1 kiloliter (kl.).

4. **Weight.** The **gram** is the weight of 1 c.c. water at 4° C.; 1 liter of water at 4° C. weighs 1 **kilogram**.

10 milligrams (mg.)	= 1 centigram (cg.).
10 centigrams	= 1 decigram (dg.).
10 decigrams	= 1 gram (g.).
1,000 grams	= 1 kilogram (kg.).

TABLE OF EQUIVALENTS.

1. Length.

1 centimeter	= 0.3937 in.
1 meter	= 39.37 in. = 3.28 ft.
1 kilometer	= 1,000 m. = 0.6214 mile.
1 inch	= 2.54 cm.
1 foot	= 0.3048 m.
1 mile	= 1.6094 km.

2. Area.

1 sq. cm.	= 0.155 sq. in.
1 sq. m.	= 10.764 sq. ft. = 1.196 sq. yd.
100 m. square	= 10,000 sq. m. = 1 hectare = 2.47 acres.
1 sq. km.	= 0.385 sq. mile.

3. Volume.

1 cu. cm.	= 0.061 cu. in.
1 cu. m.	= 35.315 cu. ft.
1 liter	= 1,000 cu. cm. = 1.0567 qt. (U. S.)

4. Weight.

1 gram	= 15.4324 grains.
1 kilogram	= 1,000 grams = 2.2046 lbs.
1 metric ton	= 1,000 kg. = 2,204.6 lbs.
1 short, or net ton	= 2,000 lbs.
1 long, or gross ton	= 2,240 lbs.
1 grain	= 0.0648 gram.
1 ounce (avoirdupois)	= 28.35 grams.
1 ounce (troy)	= 31.1 grams.

TABLE OF ATOMIC WEIGHTS AND SPECIFIC HEATS.

		H = 1.	O = 16.	
Aluminum	Al . . .	26.9	27.1	0.214
Antimony	Sb . . .	119.2	120.2	0.0508
Argon	A . . .	39.6	39.88	
Arsenic	As . . .	74.37	74.96	0.0814
Barium	Ba . . .	136.3	137.37	
Bismuth	Bi . . .	206.5	208.0	0.0308
Boron	B . . .	10.9	11.0	0.366
Bromine	Br . . .	79.35	79.92	0.0843†
Cadmium	Cd . . .	111.55	112.4	0.0567
Cæsium	Cs . . .	131.8	132.81	
Calcium	Ca . . .	39.8	40.07	0.170
Carbon	C . . .	11.9	12.00	0.459††
Cerium	Ce . . .	139.1	140.25	0.0448
Chlorine	Cl . . .	35.18	35.46	
Chromium	Cr . . .	51.6	52.0	0.100
Cobalt	Co . . .	58.53	58.97	0.107
Columbium	Cb . . .	92.8	93.5	
Copper	Cu . . .	63.08	63.57	0.0952
Dysprosium	Dy . . .	161.2	162.5	
Erbium	Er . . .	166.4	167.7	
Europium	Eu . . .	151.	152.0	
Fluorine	Fl . . .	18.9	19.0	
Gadolinium	Gd . . .	156.5	157.3	
Gallium	Ga . . .	69.5	69.9	0.079
Germanium	Ge . . .	71.9	72.5	
Glucinum	Gl . . .	9.0	9.1	0.058
Gold	Au . . .	195.7	197.2	0.0324
Helium	He . . .	3.96	3.99	
Hydrogen	H . . .	1.000	1.008.	
Indium	In . . .	113.9	114.8	0.0570
Iodine	I . . .	125.9	126.92	0.0541
Iridium	Ir . . .	191.7	193.1	0.0326
Iron	Fe . . .	55.4	55.84	0.114
Krypton	Kr . . .	82.18	82.92	
Lanthanum	La . . .	137.9	139.0	0.0449
Lead	Pb . . .	205.5	207.1	0.0314
Lithium	Li . . .	6.88	6.94	0.941
Lutecium	Lu . . .	172.6	174.0	
Magnesium	Mg . . .	24.1	24.32	0.250
Manganese	Mn . . .	54.5	54.93	0.122
Mercury	Hg . . .	199.0	200.6	0.0319†

† Solid.

†† Diamond.

TABLE OF ATOMIC WEIGHTS AND SPECIFIC HEATS.—*Continued.*

		H = 1.	O = 16.	
Molybdenum	Mo . . .	95.3	96.0	0.0722
Neodymium	Nd . . .	143.1	144.3	
Neon	Ne . . .	20.0	20.2	
Nickel	Ni . . .	58.23	58.68	0.108
Niton (radium emanation)	Nt . . .	220.6	222.4	
Nitrogen	N . . .	13.9	14.01	
Osmium	Os . . .	189.7	190.9	0.0311
Oxygen	O . . .	15.88	16.00	
Palladium	Pd . . .	105.9	106.7	0.0593
Phosphorus	P . . .	30.78	31.04	0.189*
Platinum	Pt . . .	193.6	195.2	0.0324
Potassium	K . . .	38.82	39.10	0.166
Praseodymium	Pr . . .	139.5	140.6	
Radium	Ra . . .	224.6	226.4	
Rhodium	Rh . . .	102.1	102.9	0.0580
Rubidium	Rb . . .	84.79	85.45	
Ruthenium	Ru . . .	100.9	101.7	0.0611
Samarium	Sm . . .	149.3	150.4	
Scandium	Sc . . .	43.8	44.1	
Selenium	Se . . .	78.6	79.2	0.0762†
Silicon	Si . . .	28.1	28.3	0.203†
Silver	Ag . . .	107.03	107.88	0.0570
Sodium	Na . . .	22.81	23.00	0.293
Strontium	Sr . . .	86.95	87.63	
Sulphur	S . . .	31.83	32.07	0.178††
Tantalum	Ta . . .	180.0	181.5	
Tellurium	Te . . .	126.5	127.5	0.0474
Terbium	Tr . . .	157.9	159.2	
Thallium	Tl . . .	202.4	204.0	0.0335
Thorium	Th . . .	230.6	232.4	0.0276
Thulium	Tm . . .	167.2	168.5	
Tin	Sn . . .	118.1	119.0	0.0562
Titanium	Ti . . .	47.7	48.1	0.1485
Tungsten	W . . .	182.6	184.	0.0334
Uranium	Ur . . .	237.6	238.5	0.0277
Vanadium	V . . .	50.6	51.0	
Xenon	Xe . . .	129.2	130.2	
Ytterbium	Yb . . .	170.6	172.0	
Yttrium	Y . . .	88.3	89.0	
Zinc	Zn . . .	64.87	65.37	0.0955
Zirconium	Zr . . .	89.9	90.6	0.0662

* Yellow.

† Crystalline.

†† Rhombic.

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APPENDIX.

V

TENSION OF AQUEOUS VAPOR IN MM. OF MERCURY (REGNAULT).

TEMP.	TENSION.	TEMP.	TENSION.	TEMP.	TENSION.
0° C.	4.6	11° C.	9.8	21° C.	18.5
1	4.9	12	10.4	22	19.7
2	5.3	13	11.1	23	20.9
3	5.7	14	11.9	24	22.2
4	6.1	15	12.7	25	23.6
5	6.5	16	13.5	26	25.0
6	7.0	17	14.4	27	26.5
7	7.5	18	15.4	28	28.1
8	8.0	19	16.3	29	29.8
9	8.5	20	17.4	30	31.6
10	9.1	...	...	...	...

TABLE OF SPECIFIC GRAVITIES (WATER = 1).

Acetic acid*	1.053	Lead	11.35
Alcohol (ethyl)*	0.794	Limestone	3.2
Aluminum	2.67	Lithium	0.59
Antimony	6.72	Magnesium	1.74
Arsenic	5.7	Manganese	8.0
Bismuth	9.8	Mercury†	13.596
Boron	2.63	Nickel	8.57
Brass	8.3	Nitric acid (conc.)*	1.42
Carbon (gas)	1.8	Phosphorus	1.83
Carbon disulphide*	1.27	Platinum	21.5
Chloroform*	1.5	Potassium	0.865
Coal (anthracite)	1.26 to 1.8	Silicon	2.49
Cobalt	8.8	Silver	10.57
Copper	8.9	Sodium	0.97
Diamond	3.53	Sulphur	2.03
Ether*	0.72	Sulphuric acid	1.84
Glass	2.6 to 3.6	Tin	7.29
Gold	19.3	Water at 0° C.	0.999
Hydrochloric acid (conc.)*	1.22	" " 4.07° C.	1.000
Ice	0.918	" " 100° C.	0.958
Iodine	4.95]	" (sea)	1.026
Iron	7.8	Zinc	6.9 to 7.2

* At 15° C.

† At 0° C.

WEIGHT (IN GRAMS) OF A LITER OF THE DRY GAS AT 0° C. AND 760 MM.

Air	1.293	Marsh gas	0.717
Ammonia	0.762	Nitric oxide	1.34
Carbon dioxide	1.977	Nitrogen	1.256
Carbon monoxide	1.251	Nitrous oxide	1.97
Chlorine	3.18	Oxygen	1.429
Hydrogen chloride	1.61	Sulphur dioxide	2.87
Hydrogen	0.0896	Steam	0.806
Hydrogen sulphide	1.542		

HEAT OF FORMATION AND HEAT OF SOLUTION IN
KILOGRAM CENTIGRADE UNITS (1,000 CALORIES).

NAME.	Formula.	Heat of Formation.	Heat of Solution in Water.
Ozone	O ₃	-30.	. .
Water (liquid)	H ₂ O	68.4	. .
Hydrogen peroxide	H ₂ O ₂	45.2	. .
Hydrogen chloride	HCl	22.	17.3
Hydrogen bromide	HBr	12.	19.9
Hydrogen iodide	HI	-6.1	19.2
Hydrogen sulphide	H ₂ S	2.7	4.6
Sulphur dioxide	SO ₂	71.	7.7
Sulphuric acid	H ₂ SO ₄	193.1	17.8
Ammonia	NH ₃	12.	8.4
Nitrogen tetroxide	N ₂ O ₄	-2.6	. .
Nitrogen dioxide	NO ₂	-7.7	. .
Nitric oxide	NO	-21.6	. .
Carbon disulphide	CS ₂	-19.6	. .
Carbon dioxide	CO ₂	97.	. .
Carbon monoxide	CO	29.	. .
Phosphorus, red, from yellow form		27.3	. .
Phosphorus pentoxide	P ₂ O ₅	370.	36.
Potassium hydroxide	KOH	103.2	13.3
Potassium carbonate	K ₂ CO ₃	281.	6.5
Potassium nitrate	KNO ₃	119.	-8.5
Sodium chloride	NaCl	97.6	-1.2
Sodium hydroxide	NaOH	102.	9.9
Sodium carbonate	Na ₂ CO ₃	272.6	5.6
Ammonium chloride	NH ₄ Cl	75.8	-4.
Calcium hydroxide	Ca (OH) ₂	215.	3.
Magnesium hydroxide	Mg (OH) ₂	217.	. .
Aluminum hydroxide	Al (OH) ₃	297.	. .
Ferric hydroxide	Fe (OH) ₃	198.	. .
Ferrous-ferric oxide	Fe ₃ O ₄	265.	. .
Zinc oxide	ZnO	86.	. .
Cupric oxide	CuO	37.	. .
Mercuric oxide	HgO	20.7	. .
Silver oxide	Ag ₂ O	6.	. .
Lead monoxide	PbO	50.	. .

QUALITATIVE SOLUBILITY OF THE COMMON SALTS, ETC.

	Acetates.	Arsenates.	Arsenites.	Borates.	Bromides.	Carbonates.	Chlorates.	Chlorides.	Chromates.	Cyanides.	Ferrieyanides.	Ferrocyanides.	Fluorides.	Hydroxides.	Iodides.	Nitrates.	Oxalates.	Oxides.	Phosphates.	Silicates.	Sulphates.	Sulphides.	Tartrates.
Al	W	W	W	A	W	W	W	W	W	W	W	W	W	A	W	W	W	A	A	W	W	A	W
NH ₄	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Sb	W	W	W	A	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	A
Ba	W	W	W	A	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	A
Bi	W	W	W	A	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	A
Cd	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Ca	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Cr	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Co	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Cu	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Au	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
H	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Fe ⁱⁱ	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Fe ⁱⁱⁱ	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Pb	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Mg	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Mn	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Hg ^{cl}	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Hg ^u	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Ni	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
K	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Ag	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Na	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Sn ⁱⁱⁱ	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Sn ⁱⁱ	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Sr	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W
Zn	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	A	A	W	W	A	W

W=soluble in water; A=insoluble in water, but soluble in acids; sw=sparingly soluble in water, but soluble in acids; sa=insoluble in water, and only sparingly soluble in acids; I=insoluble in both water and acids.

APPROXIMATE SOLUBILITY, IN GRAMS, IN 100 GRAMS OF WATER AT
ORDINARY TEMPERATURE.

	Fluoride.	Chloride.	Bromide.	Iodide.	Chlo- rate. mate.	Io- date.	Ni- trate.	Sul- phate.	Carbo- nate.	Chro- mate.	Hydrox- ide.
Ammonium .	—	36.4	73.3	166.	—	—	175.	75.	27.	—	—
Barium . .	0.16	37.	104.	201.	35.4	0.8	8.7	.00023	.0023	.0004	3.7
Calcium . .	.0016	73.2	143.	200.	179.	85.	122.	0.2	.0013	0.4	0.17
Lead . . .	0.07	1.5	0.6	0.08	150.	1.3	.002	0.004	.0001	.0002	0.01
Magnesium .	.0076	56.	103.	148.	126.	43.	6.9	74.3	0.1	73.	0.001
Mercuric . .	—	7.2	1.2	0.004	—	0.15	—	—	—	—	—
Potassium .	93.	33.	66.	137.	6.6	6.4	7.6	30.	108.	63.	143.
Silver . . .	195.	.00016	.00001	.0000003	12.3	0.59	.004	0.55	0.003	.0025	0.01
Sodium . .	4.4	36.	89.	178.	97.	37.	8.3	84.	19.4	61.	116.
Strontium .	0.012	51.	97.	169.	173.	30.	0.25	66.3	.0011	0.12	0.77
Zinc . . .	0.005	204.	478.	419.	184.	58.	0.83	118.	0.004	—	.0005

100 C.C. OF A GAS AT THE TEMPERATURES AND PRESSURES GIVEN, REDUCED
TO 0° C. AND 760 MM.

TEMP.	PRESSURE IN MILLIMETERS OF MERCURY.										
	720	725	730	735	740	745	750	755	760	765	770
15° C.	89.79	90.42	91.04	91.67	92.29	92.91	93.54	94.16	94.78	95.41	96.03
16°	89.48	90.11	90.73	91.35	91.97	92.59	93.21	93.83	94.45	95.08	95.70
17°	89.17	89.79	90.41	91.03	91.66	92.27	92.89	93.51	94.13	94.75	95.37
18°	88.87	89.48	90.10	90.72	91.34	91.97	92.57	93.19	93.80	94.42	95.04
19°	88.57	89.18	89.79	90.41	91.03	91.66	92.26	92.87	93.48	94.10	94.71
20°	88.26	88.87	89.48	90.10	90.72	91.34	91.94	92.55	93.16	93.78	94.39
21°	87.96	88.57	89.18	89.79	90.41	91.02	91.63	92.24	92.85	93.46	94.07
22°	87.66	88.27	88.87	89.48	90.10	90.72	91.31	91.93	92.53	93.14	93.75
23°	87.36	87.97	88.57	89.18	89.79	90.41	91.00	91.61	92.22	92.82	93.43
24°	87.07	87.67	88.27	88.87	89.48	90.09	90.69	91.31	91.91	92.51	93.11
25°	86.78	87.38	87.98	88.58	89.19	89.79	90.39	91.00	91.60	92.20	92.80

LIST OF THE METALS IN THE ORDER OF DECREASING SOLUTION TENSION.

The Alkali Metals.	Lead.
The Alkaline-Earth Metals.	Hydrogen.
Magnesium.	Bismuth.
Aluminum.	Antimony.
Manganese.	Copper.
Zinc.	Arsenic.
Cadmium.	Mercury.
Iron.	Silver.
Cobalt.	Palladium.
Nickel.	Platinum.
Tin.	Gold.

The metals appearing first in the table can replace those that follow, in the solutions of their salts.

CRYSTAL FORMS.

Crystals are the forms assumed by most solid substances. They are bounded by plane faces, which express *outwardly* a regular arrangement of the molecules within. **Six systems** of crystals are distinguished:—

1. Isometric, or regular.
2. Quadratic, or tetragonal.
3. Hexagonal.
4. Orthorhombic, or rhombic.
5. Monoclinic, or monosymmetric.
6. Triclinic, or asymmetric.

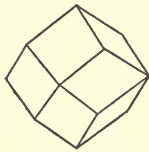
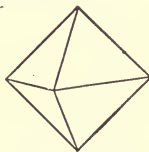
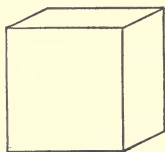


FIG. A.

This classification is based upon the relations between **three** (in one case, *four*) lines, or **axes**, which determine the positions of the crystal faces.

1. Isometric System. In this system the *three axes are at right angles, and are equal*. Fig. A shows three isometric solids: the *cube*, the *octahedron*, and the *dodekahedron*. Salt, alum, potassium iodide, galena, iron pyrites, and the diamond crystallize in this system.

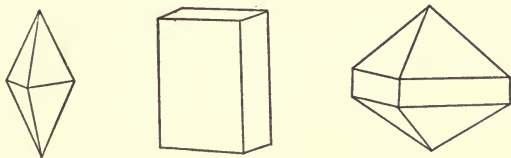


FIG. B.

2. Quadratic System. The crystals of the quadratic system (Fig. B) have three axes at right angles, but only two are of equal length.

3. Hexagonal System. This system has **four axes**, three of them equal and in the same horizontal plane. Fig. C gives two illustrations. The three equal axes bisect one another so as to form 60° angles. The fourth axis is perpendicular to the plane of the other three, at the point of their intersection. The prism, pyramid, and rhombohedron belong to this system. Substances crystallizing in the forms of the system are quartz, ice, and limestone.

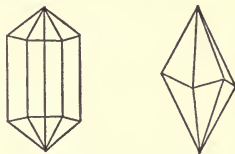


FIG. C.



FIG. D.

4. Rhombic System. Here there are three axes, all at right angles, but *no two are of equal length*. Sulphur (Fig. 55), potassium nitrate (Fig. D), and the garnet crystallize in this system.



FIG. E.

5. Monoclinic System. In this system there are three axes of unequal length. Each one bisects the other two, but only two of the axes are at right angles (Fig. E). Gypsum, monoclinic sulphur, rock candy (Fig. E, 2), and Glauber's salt belong to this system.

6. Triclinic System. Crystals of the triclinic system have three axes of unequal length, and the intersecting angles are all oblique and unequal. Blue vitriol (Fig. F) and potassium dichromate crystals belong in this system.

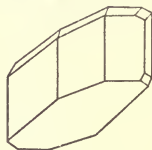


FIG. F.

CORRECTION OF BAROMETER READING FOR TEMPERATURE.

To find the height which the barometer would have at 0°C . (cf. § 43, text) subtract the proper "Correction" from the reading of the barometer, *in millimeters*.

TEMPERATURE, $^{\circ}\text{C}$.	CORRECTION, IN MM.	TEMPERATURE, $^{\circ}\text{C}$.	CORRECTION, IN MM.	TEMPERATURE, $^{\circ}\text{C}$.	CORRECTION, IN MM.
12°	1.6	17°	2.2	23°	3.0
13°	1.7	18.5°	2.4	24.5°	3.2
14°	1.8	19°	2.5	25°	3.3
15°	2.0	20°	2.6	26°	3.4
16°	2.1	21.5°	2.8	27°	3.5

THE SPECTROSCOPE AND SPECTRUM ANALYSIS.

When white light is passed through a narrow opening, such as a **slit**, and then through a glass **prism**, the light is broken up

into its **primary colors**, *violet, indigo, blue, green, yellow, orange, and red (VIBGYOR)*. The waves producing *violet* light are the shortest, those producing *red* light, the longest. The prism separates white light into colored rays because it *bends*, or **refracts**, the short waves more than it does those of greater length. Hence the *violet* rays are bent **most**, and the *red* rays **least**. After refraction, the beam of white light appears as a **band**, made up of *colored images of the slit* placed side by side. This band is called a **spectrum**.

The **spectroscope** (Fig. G) is an apparatus devised by Bunsen and Kirchhoff, in 1859, for studying spectra. It consists of a prism (*P*) contained in the central part of the instrument (when in use, this is covered) and the three tubes (*A*), (*B*), and (*C*). (*A*) contains lenses, which gather the light rays admitted through the narrow slit (*S*) and direct them to the prism (*P*). The observer looks through the telescope (*C*). This magnifies the images of the slit which together make up the spectrum. The tube (*B*) contains a scale, which is illuminated by a candle or other light. The spectrum and the magnified scale are seen together, and the parts of the spectrum can thus be designated by their positions on the scale.

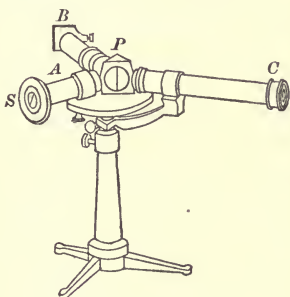


FIG. G.

We have seen (*cf.* §§ 419 and 420) that *volatile* potassium compounds give a violet color to the Bunsen flame, while sodium compounds make it yellow. When a sodium salt is placed in a Bunsen flame, before the slit of an ordinary spectroscope, the yellow color is confined to a single bright line. This is located at a definite place in what forms the yellow part of the spectrum of white light. Potassium, on the other hand, gives two red

lines at one end of the spectrum, and a violet line at the other end. Both of these elements can thus be readily detected in a mixture. The same is true of other mixtures of elements: each element has its own lines, in definite parts of the spectrum, regardless of the presence of others. It has been found that $\frac{1}{3}$ of a gram of sodium can be detected by the spectroscope.

The light given off by incandescent **solids** or liquids (*cf.* § 302) produces a **continuous spectrum**, but the spectra of incandescent **gases**, like the vapors of sodium and potassium, are **bright-line spectra**: they are made up of bright, colored lines separated by dark spaces. When light from an incandescent *solid* substance passes through the **vapor** of the same substance, the lines are in their proper places in the spectrum, but they are **dark**. We call such spectra **absorption spectra**. The spectrum of sunlight is a continuous spectrum crossed by dark lines (" **Fraunhofer's lines** ") which are in the positions belonging to many well known terrestrial elements. Hence we argue that these elements of our earth are also present in the sun. The light from the solid or liquid substances in the *photosphere* of the sun passes through the vapors of the same substances in the sun's *atmosphere*; hence an **absorption spectrum** is produced. The light of many stars has properties like those of sunlight.

The Bunsen flame is not hot enough to volatilize the salts of many metals; for these the electric arc may be used. This produces a **spark spectrum**. The spectrum of a **gas** is obtained by sealing the gas in a glass tube provided with electrodes, reducing the pressure with a vacuum pump, and passing an electric discharge through the gas.

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LABORATORY EXERCISES

FROM

THE "ESSENTIALS OF CHEMISTRY"

BY

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PREFATORY NOTE.

These laboratory exercises form a part of the "Essentials of Chemistry," and contain specific directions for laboratory work. All the exercises are intended *for the student*, and are so arranged that they may be used in schools having either one-hour or two-hour laboratory periods.

The experiments require only **common materials** and **simple apparatus**. The quantities of materials have been stated definitely and accurately. Where possible, the directions call for fractional parts of a test tube, so that unnecessary weighing may be avoided. The test tube meant is the ordinary $5 \times \frac{5}{8}$ inch tube found in most laboratories.

In the revised edition of the laboratory exercises the order of the experiments has been altered to bring it into harmony with the revised text. Many of the experiments have been rewritten, and several new ones have been added. The *quantitative* exercises are not numerous. They have been selected for their importance in showing the weight relations of chemical reactions. All have been thoroughly tested, and have succeeded in the hands of *average* students. For the *earlier* quantitative experiments the **object** of the experiment and the **method** used have been described briefly at the beginning of the exercise, so that the student may have a better appreciation of the directions he is to follow and of the result sought.

PREFATORY NOTE.

The reviser will be glad to learn of any errors that may exist in the exercises, and to receive suggestions from persons interested.

AUGUST, 1912.

J. C. H.

LABORATORY DIRECTIONS.

(For the Student.)

1. Provide yourself with an apron and a pair of sleeves (rubber is the best material for these); also with soap and towel, and a white cloth about a yard square. The cloth is to be used for wiping apparatus.

2. Work by yourself; and give *your own* descriptions, observations, and calculations, not those of *another*.

3. Record *at once* all the observations you make in connection with an experiment. See that your notes contain the answer to every question, direct or implied, that occurs in the laboratory exercise. Write neatly and distinctly. If the notes of two experiments occur on the same page, separate them by at least two centimeters of space.

4. Have a place for everything. Throw away nothing until you are sure you are through with it. Throw nothing but liquids into the sink. Put other waste materials into the proper receptacle.

5. If an experiment is unsatisfactory, repeat it until you are successful; but *first* learn the probable cause of your error.

6. When you enter the laboratory, examine your table, and see that everything has been left as it should be by the persons who share the table with you. If anything is wrong, report the fact *at once* to the instructor.

When you leave, see that the water and the gas are turned off, and that everything on your table is in good order.



LABORATORY EXERCISES.

EXPERIMENT I.

THE BUNSEN BURNER.

Apparatus. — Bunsen burner, test tube, test-tube holder (see note below).

Materials. — Matches, water.

a. Examine carefully the Bunsen burner on your desk. Take it apart, and draw a sketch of each part.

b. Put the burner together, close the holes at the base, and connect with gas supply.

To light the burner, turn on the gas and then hold a lighted match near the side of the burner and about one-half a centimeter below its mouth. Note the character of the flame; is it luminous or not? Now open the holes carefully until the luminous region has just disappeared. This is the "Bunsen" flame. For most work it should be 7 to 10 centimeters (3 to 4 inches) high. The holes of the burner should be open far enough to prevent a deposit of soot upon the object heated, but not far enough to cause the flame to make a noise.

c. Introduce quickly into the center of the Bunsen flame, one-half a centimeter above the burner, the head end of a match. Result? Is the gas in this region burning?

To heat an object effectively, place it higher up in the flame; the best place is just above the apex of the dark, inner cone of unburned gas. Locate this region.

d. Put 5 c.c. water into a test tube, and make a note of the height of the column of water in centimeters. Whenever you are asked to take 2, 5, 10, etc., cubic centimeters of anything, refer to this experiment, and use the length of the column just measured as your *unit*.

e. Heat the water in the test tube to boiling. To do this properly have the outside of the tube *dry*; hold the tube in the holder, and incline the tube at an angle of about 45° to the table top. Then introduce the bottom of the tube into the effective region (cf. c) of the flame. *Heat only the part of the tube containing the liquid*; if the flame strikes the glass above the liquid level, the tube may crack.

Do not hold the tube still, but move it gently in the flame. When boiling begins, raise the tube a little above the flame,—always keeping it inclined,—so that the water may not “boil over.”

f. *These directions are general*, and will apply whenever you heat liquids in test tubes.

Note.—A very convenient test-tube holder can be made by folding a piece of writing paper twice, so as to produce a strip about 1 cm. wide and 10 to 15 cm. long. This is placed about the tube like a holder. The free ends are held together close to the tube.

EXPERIMENT II.

MANIPULATING GLASS TUBING.

Apparatus. — Bunsen burner, "wing-top" or illuminating gas burner, file, blast-lamp.

Materials. — Piece of soft glass tubing more than 15 cm. long, one of ignition tubing 18–20 cm. long.

a. Cut off a piece of glass tubing 15 cm. long. To do this, make on the tubing a file mark in a plane perpendicular to the length of the tubing; grasp the tube in both hands, and place the thumb nails together opposite the scratch. By *pushing gently with the thumbs* and at the same time *pulling with the hands* you will succeed in breaking the tubing so that the ends are fairly regular.

b. Round off ("fire-polish") both ends of the 15 cm. tube by turning them about in the Bunsen flame until the edges become red hot. Let the ends cool.

c. Bend the 15 cm. tube at its middle into the form of a right angle. For this purpose use a *flat* Bunsen flame — produced by a "wing-top" attachment — or a flat illuminating flame.

Take the tube in both hands, one at each end, and hold its central part *lengthwise with* and *over* the flat flame. At the same time twirl the tube between thumbs and forefingers. Then lower the tube — keep turning it — into the upper part of the flame, and heat until you find that the glass is fairly soft. Then bend *gently* to a right angle.

d. If you used the Bunsen flame, *anneal* the glass at the bend by closing the holes of the burner and allowing

the hot glass to cool first in the *smoky* flame. When the bend is covered with soot, support it so that it will not touch a cold object. When the tube is cold, wipe off the soot.

e. Make two "ignition tubes" of hard glass by melting a piece of hard glass tubing 18–20 cm. long at its middle in the flame of a blast-lamp. Do this by grasping one end of the tubing between the thumb and forefinger of each hand, and twirling it rapidly in the flame until the glass softens and the walls of the tubing come close together. Then draw the two halves apart, but do not break the connection until the glass becomes stiff. Now break the connecting tube, and melt off the drawn-out glass where the tube becomes narrow. For this use a **small** blast-lamp flame. When the closed end of the ignition tube is cool, "fire-polish" the open end in the blast-lamp flame.

EXPERIMENT III.

SOLUTION, FILTRATION, AND EVAPORATION.

Apparatus. — Glass rod 15 cm. long (unfinished), file, two beakers of about 50 c.c. capacity, ring stand, wire gauze, funnel, funnel support (small ring of ring stand), evaporating dish, test tubes, mortar.

Materials. — Marble, salt, dilute hydrochloric acid, filter paper.

a. Make a glass stirring rod 15 cm. long, cutting off a piece from a larger one, just as in Experiment II, *a*. Round off both ends in the flame.

Taste a bit of marble, then put it into a test tube and add a drop of dilute hydrochloric acid. Results? Do the same with a pinch of salt, and state results. How can you distinguish marble from salt?

b. In a mortar powder a lump of marble, add to it about $\frac{1}{6}$ of a test tube of salt, and grind the two thoroughly together. Put the mixture into a beaker with about 20 c.c. cold water, and heat the beaker over the flame until its contents boil. Before heating the beaker see that it is *dry* on the outside, then place it upon a wire gauze supported on the ring stand. Move the flame about under the gauze until the beaker has become *warm*; then put the burner under the center of the beaker. The height of the gauze above the burner should be so great that the bottom of the beaker may be a little above the apex of the dark inner region of the flame.

Note. — *Always follow these directions* when you are heating a beaker, an evaporating dish, or a flask, unless there is some special reason for not doing so. What becomes of the salt? Of the marble?

c. Next, *filter* the solution. You need a funnel, a support (see above), a filter, the glass rod made in *a*, and a second beaker.

Fold the circular filter twice in lines at right angles to each other. Press the folded edges between thumb and forefinger, but *not* between the nails. Open the filter so that it shall form an inverted cone which just *fits* the funnel. One-half of the conical surface is made up of three of the quarters into

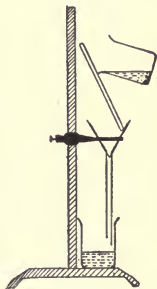


FIG. 93.

which the paper was folded; the remaining quarter of the paper makes up the other half of the cone.

d. Hold the filter in place in the funnel, and wet it completely; it should adhere everywhere to the inner surface of the funnel, and its point should extend a little into the stem of the funnel.

Pour the salt solution down the glass rod to the filter.

The glass rod should touch the lip of the beaker; and the stem of the funnel should touch the side of the beaker beneath it.

Always follow these directions in filtering an insoluble solid from a solution.

e. Does anything remain on the filter? We call it the *residue*. What passes through is the *filtrate*. Test the residue as you did the marble and salt in *a*. What is it?

A substance which remains *mixed* with a liquid, but not dissolved in it, is said to be "suspended in," or "held in suspension by" the liquid.

A *suspended* substance becomes, after filtration, a *residue*.

f. Pour the filtrate of *c* into an evaporating dish, and heat (for precautions, cf. *b*) over the flame. Boil off the water until a solid begins to separate out; then set the dish aside until it is cold, or until the next laboratory period. What is the solid obtained?

Is this separation of the salt from the marble a physical or a chemical operation?

EXPERIMENT IV.

EFFECT OF HEAT UPON OXIDES.

Apparatus. — Small ignition tube of hard glass, rubber connecting tube, delivery tube, pneumatic trough, test tube, ring stand, clamp.

Materials. — Pine splinter, mercuric oxide, lead dioxide.

a. In a small tube of hard glass sealed at one end and about 10 cm. long — “ignition tube” — place a layer of mercuric oxide *not more than* one-half a centimeter thick.

In a basin containing water, invert a test tube of water. See that no air bubbles remain in the test tube. Vessels

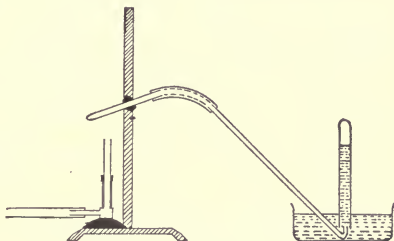


FIG. 94.

for holding water over which gases are collected are called “pneumatic troughs.”

Attach to the ignition tube by means of a piece of rubber tubing a delivery tube long enough to reach to the bottom of the pneumatic trough. Support the ignition and delivery tubes so that the closed end of the ignition tube is only a little lower than its other end, and so that the mercuric oxide may be heated in the hot portion of the Bunsen flame.

b. *Begin to heat slowly*, keeping the flame in motion. Note any change in color of the oxide. Afterward heat

strongly with a steady flame until all of the powder disappears. Collect *over water* anything that escapes from the delivery tube by allowing it to displace the water of the test tube. When the operation is over, *remove the delivery tube from the water before removing the flame*. Why?

c. Cover the mouth of the test tube under water with the thumb, remove tube from water, invert, and introduce a pine splinter with a *spark* on the end of it. Result? Is the gas in the test tube *air*? What is it?

d. When the ignition tube is cool, invert it and strike its open end sharply against the table. Result? What substance is this? On what part of the tube did it collect? Why did it not pass out of the tube?

e. Would you call this a chemical change, or not? How is mercuric oxide made? Consult a text.

f. Repeat *a*, *b*, *c*, and *d*, using **lead dioxide** instead of mercuric oxide. Does the powder disappear? Does it give off a gas? What is the gas? What is the residue? Answer *e* for this case also.

EXPERIMENT V.

OXYGEN.

Apparatus. — Mortar and pestle (?), test tubes, ring stand and clamp, one-holed stopper, delivery tube, pneumatic trough, 4 collecting bottles, glass or cardboard cover, deflagration spoon.

Materials. — Powdered potassium chlorate and manganese dioxide, pine splinter, sulphur, iron wire (picture cord) at least 15 cm. long, lime-water, magnesium wire or ribbon.

a. On a *clean* piece of writing paper mix carefully 6–8 c.c. powdered potassium chlorate with about 3 c.c. powdered manganese dioxide. If the substances are not found in powdered form in the laboratory, grind them *separately*, in *clean* mortars, before mixing.

b. Before you use the whole mixture, test the quality of a sample (1 c.c.) by heating it gently in an *open* test tube. If there is any evidence of *violent combustion*, or if *large* sparks appear, reject the mixture, and make a fresh one. A few *small* sparks indicate only traces of dust, etc.

c. If the mixture is satisfactory, put it into a test tube supported by a clamp attached to a ring stand. The test tube is then fitted with a one-holed stopper and a delivery tube reaching under water in a pneumatic trough.

Have 4 bottles filled with water and inverted in the trough.

To invert bottles in the trough without letting in air, fill them to overflowing with water, cover their mouths with slips of glass or cardboard, press the latter against the bottle, and invert quickly under water. Then remove the covers.

To remove a bottle full of gas from water, slip under the mouth of the bottle, *under water*, a glass or cardboard cover, and hold it in place as before. Leave a filled bottle with its mouth under water until used, if possible.

Whether a bottle of gas shall be placed *upright* or *inverted* upon the table depends upon the *specific gravity* of the gas.

d. Heat the test tube *gently* from the top of the mixture *downward*. Regulate the flame so as to keep the

evolution of gas *steady, but not violent*. Keep the flame *in motion*, so as not to soften the glass.

When the collecting bottles are full, *first* take the delivery tube out of the water, and *then* remove the flame. Why this precaution?

The gas is **oxygen**.

e. Into one bottle of the gas put a glowing splinter as in Experiment IV, c. Result? Gradually lower the splinter into the bottle until combustion stops. What becomes of the splinter? Of the oxygen?

To the contents of the bottle add 5 c.c. calcium hydroxide solution (lime-water), cover with the hand, and shake vigorously. Result?

N.B. Lime-water reacts with **carbon dioxide** to give a white, insoluble solid, **calcium carbonate**. This serves as a **test** for carbon dioxide. Where does the carbon of the carbon dioxide come from?

f. Note the odor of the gas in the second bottle. Then put into the bottle a deflagrating spoon containing burning sulphur. Light the sulphur by holding the spoon in a flame.

Have a cardboard cover with a small hole for the handle of the deflagrating spoon, and keep the bottle covered until combustion stops. Results?

What becomes of the sulphur? Of the oxygen? Note the odor of the gas now in the bottle. Does this gas support the combustion of a splinter? Try it. Name the gas. Add 5 c.c. of water to the bottle, shake it about, and then put in one piece each of red and blue litmus paper. Result?

g. Have the third bottle of oxygen covered and set upright on the table. Draw aside the cover for a moment

while you pour in sand enough to cover the bottom of the bottle; then replace the cover.

Melt some sulphur in a deflagrating spoon, and dip into it one end of a piece of iron picture cord. Light the sulphur tip, and *at once* hold the iron wire in the bottle of oxygen. Result? Keep the wire in the gas until action ceases. Describe the product and name it. Why was the iron tipped with sulphur?

h. Hold a piece of magnesium wire or ribbon by means of iron tongs, or make a hook upon it, and hang it on the reverse end of a file. Light it in the Bunsen flame, and hold it in the fourth bottle of oxygen. Result? Name and describe the product. Add a few drops (not more) of water to the product in the bottle, and then bring into contact with it one piece each of red and blue litmus paper. Let them remain some time. Which one is changed? Compare with the result in *f*.

EXPERIMENT VI.

PER CENT OF OXYGEN IN POTASSIUM CHLORATE.

Apparatus. — Hard glass test tube, Bunsen burner, clamp, and ring stand.

Materials. — Pure, powdered potassium chlorate which has been dried in an air bath at 120° C.

a. The **object of this experiment** is given in the title. It is attained by decomposing completely a weighed amount of pure, dry potassium chlorate and weighing the potassium **chloride** that remains. The material lost is *oxygen*.

b. Weigh a clean, dry hard-glass test tube accurately,

and put into it about 5 c.c. (a layer 1 inch thick) of the potassium chlorate. Wipe off any particles that may adhere to the mouth of the test tube. Weigh the test tube and chlorate accurately, and record the weights as directed in § *d*.

c. Support the test tube of *b* by means of a clamp and a ring stand, keeping the open end of the test tube a little higher than the closed one. Have the clamp near the **open** end. Begin to apply heat *cautiously*, with a small, moving flame. Then heat more strongly, until all the chlorate melts, and the melted substance is in effervescence. Do not let the effervescence become so rapid that *much* white smoke is driven out of the test tube. When all effervescence seems to have stopped, heat more strongly still, so that every part of the contents is completely melted and ceases to effervesce. Then let the tube cool, weigh it, and record the result. To make certain that the decomposition is complete, heat the tube again, cautiously at first, then strongly, and weigh the tube once more. Continue this until there is no difference between successive weighings. We call this "**heating to constant weight.**" Use the **last** weight in calculating results.

d. Record the results as follows: —

	<i>Grams.</i>
Wt. of test tube + potassium chlorate	=
" " " " alone	=
" " potassium chlorate taken	=
Wt. of test tube + potassium chlorate	=
" " " " + " chloride	=
∴ The wt. of oxygen evolved	=
Per cent of oxygen =	

EXPERIMENT VII.

KINDLING TEMPERATURE.

Apparatus. — Wire gauze at least 15 cm. square, Bunsen burner, tongs.

Material. — Matches.

a. Hold the wire gauze, by means of your tongs, 7 cm. *above* the Bunsen burner. Have the holes of the burner *open* as for the Bunsen flame. Now turn on the gas and bring a burning match *from above* down to the center of the gauze. Result?

Why does not the gas *below* the gauze take fire? Is there gas below the gauze? Prove it.

b. Let the gauze cool; and then bring it down upon the Bunsen flame until the gauze is 6 to 7 cm. above the top of the burner. Result? Hold the gauze in place until it becomes red hot. Result? Explain.

EXPERIMENT VIII.

HYDROGEN.

Apparatus. — Generating flask, or bottle of 250 c.c. capacity, two-holed stopper, funnel tube, right-angled tube, rubber connector, delivery tube, pneumatic trough, squares of glass or of cardboard, two or more wide-mouth collecting bottles (250 c.c.).

Materials. — Zinc, dilute sulphuric acid (one part by volume of acid to four volumes of water), pine splinter, cupric sulphate solution.

a. To a 250 c.c. bottle containing enough zinc to cover the bottom fit a two-holed stopper. One of the holes is for a funnel tube reaching to within one-half a centimeter of the bottom of the bottle when the stopper is in place; the other hole contains a bent tube attached by a rubber connector to a delivery tube. The delivery tube reaches to a pneumatic trough containing two bottles filled with water and inverted.

b. **Caution.** — **Keep all flames at least one meter (about three feet) away from apparatus in which hydrogen is made.**

c. See that the stopper of the generating bottle is *tight*, and add enough of the dilute sulphuric acid to immerse the lower end of the funnel tube.

Tell what takes place in bottle, funnel tube, and pneumatic trough. Explain each phenomenon. If action is not vigorous add a few drops of copper sulphate solution. Result? If evolution of gas ceases or becomes slow before you are through, add more acid. The gas produced is *hydrogen*.

d. Fill the two bottles with the gas and refill them after using. Reject the first bottleful collected by turning it mouth upward. Why not use it? Why turn it mouth upward?

Keep the second bottle inverted and introduce into its middle part a burning pine splinter 15 to 20 cm. long. Hold the splinter steady 20 to 30 seconds. Result? Does the gas burn? Where? Does the splinter continue to burn in the hydrogen? Is hydrogen combustible or a supporter of combustion?

Turn a third bottle of the gas mouth upward one minute, and repeat the test with the burning splinter.

Results? From the result compare the specific gravity of hydrogen with that of air.

e. Place the mouth of a fourth bottle of gas over the mouth of an upright bottle of air. Hold the bottles together and reverse their positions. After one minute apply a lighted match to the lower bottle. Result? To the upper. Result? What conclusion as to the diffusibility of hydrogen?

f. Have a fifth (and last) bottle only half full of gas; incline it, and then raise it slowly from the water so that air displaces the remaining water. Carry bottle, mouth down, to a flame. Result? Explain difference between this result and the combustion of hydrogen free from air.

g. From the experiment tell whether hydrogen is very soluble in water, or not.

h. Pour the liquid and the unused zinc from the bottle into a beaker. If the zinc has all dissolved, or if there seems to be enough acid to dissolve all of it, add more zinc. Leave until action ceases.

i. Examine the beaker; has anything separated from solution? If so, re-dissolve it by heating the beaker on the wire gauze, and filter hot. (*Care!*)

Collect the filtrate in another beaker or an evaporating dish, and let it stand some hours. Result?

The substance you obtain is crystallized *zinc sulphate*.

EXPERIMENT IX.

BURNING OF HYDROGEN AND REDUCTION OF
OXIDES.

Apparatus. — Hydrogen generating bottle of Experiment VIII, two-hole stopper, funnel tube, right-angle tube, rubber connector, a second right-angle tube of slightly larger diameter than the other, beaker, and test tube.

Materials. — Zinc, dilute sulphuric acid, cupric sulphate solution, cupric oxide (in wire form if possible).

a. Arrange the apparatus of Fig. 95. Into the longer (horizontal) arm of the second right-angle tube (B)

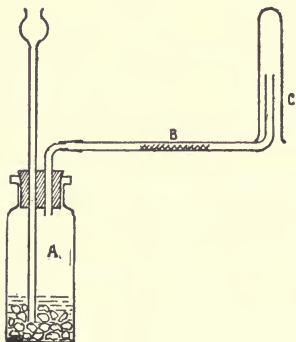


FIG. 95.

put cupric oxide in wire form. To the zinc in the generating bottle (A) add a few drops of cupric sulphate solution, then dilute sulphuric acid. When the gas comes off readily, hold over the end of the exit tube (C) a cold, clean beaker. Does any deposit of moisture appear?

b. Over the end of C invert a test tube, and after a minute carry it, mouth down, to a flame at least 4 feet away. Note what happens, and *at once* return the test tube, still mouth down, to the jet C. Continue until the hydrogen is lighted at C (consult § 50, pg. 41, of text). What is the color of the hydrogen flame *at first*?

After the end of *C* has become hot? For the reason, *cf.* § 411 of text. Hold a cold beaker over the hydrogen flame. Is there a deposit now? What is it? How was it formed?

c. While the hydrogen flame is burning, heat the tube at *B*, under the cupric oxide, first with a moving flame, then more strongly. Do not heat it enough to melt the glass.

What change occurs in the cupric oxide? What is the solid substance left? Is there any deposit in the tube? What is it? What was the source of the oxygen when hydrogen **burned**? When it was passed over cupric oxide? Define **reduction**.

EXPERIMENT X.

EQUIVALENT WEIGHT OF MAGNESIUM.

Apparatus. — Balances, pneumatic trough, wide-mouth bottle (250 c.c.), graduated jar, glass or cardboard cover.

Materials. — Magnesium wire, dilute sulphuric acid.

a. The **object of this experiment** is to find how many grams of magnesium replace **1.008** grams of hydrogen. The resulting number is called the **equivalent weight** of magnesium. The weight of the hydrogen is calculated from the volume. The volume actually obtained is "reduced" to 0° C. and 760 mm. From this we get the weight, for 1 l. of hydrogen at 0° C. and 760 mm. weighs 0.09 gram (*cf.* Appendix v):

b. In a pneumatic trough containing water to the

depth of about 3 cm. place a piece of magnesium wire the exact weight of which is known. There should be not more than 0.2 gram.

Get the exact capacity in cubic centimeters of a wide-mouth bottle by *filling* it with water and pouring the water into a graduated vessel. The bottle should hold at least 250 c.c.

c. Half fill the bottle with dilute sulphuric acid, then add enough water to fill it, and invert it in the pneumatic trough as far from the magnesium as possible. See that the bottle is free from air bubbles. Now slide the mouth of the bottle, under water, over the magnesium. Result?

d. When all the metal has disappeared, let the collected gas cool to room temperature for 5 minutes. Then add water of room temperature to the bowl, *if necessary*, so that the level of water in bottle and bowl shall be the same. Why?

Protect the bottle from the heat of the hand by grasping it with a towel; then slip under its mouth a glass or cardboard cover, and invert *quickly*, so as to lose none of the water in the bottle.

Bring a flame to the mouth of the bottle *at once*. Result?

The gas is *hydrogen*. The other product of the reaction is magnesium sulphate; it remains in solution.

Let your thermometer remain in the solution in the bottle for five minutes; then read it, and call this the **temperature** of the hydrogen. Also read the **barometer**.

e. Get the volume of the water remaining in the bottle by means of a graduated vessel. Then obtain the volume of the hydrogen *by difference*. From the reading

of the barometer, *in millimeters*, subtract the "tension of water vapor," to get the partial pressure of the **dry** hydrogen, and then reduce the volume of the hydrogen to standard conditions.

f. Calculate the **weight** of the hydrogen, and solve the following proportion for x , the **equivalent weight** of magnesium.

$$\text{Wt. of magnesium} : \text{Wt. of hydrogen} :: x : 1.008.$$

g. **Record your results** as follows:—

Wt. of magnesium taken	=	g.
Vol. of hydrogen obtained	=	c.c.
Temperature	=	° C.
Barometer reading	=	mm.
Tension of water vapor at ° C.	=	mm.
. . . Partial pressure of dry gas	=	mm.
Vol. of dry hydrogen at 0° C. and 760 mm.	=	c.c.
Wt. of dry hydrogen	=	g.
Equivalent weight of magnesium =		

EXPERIMENT XI.

PHYSICAL PROPERTIES OF WATER.

Apparatus. — Ring stand, wire gauze, 100 c.c. flask, one-hole cork stopper, doubly bent delivery tube, test tube, beaker, Bunsen burner, thermometer, evaporating dish.

Materials. — Hydrant or well water, distilled water, salt, crushed or chipped ice.

a. Distillation of Water. Set up the apparatus of Fig. 96. Half fill the flask with hydrant water, support it on the wire gauze, and attach the doubly bent delivery tube. This reaches to a test tube standing in a beaker (or bottle) of cold water.

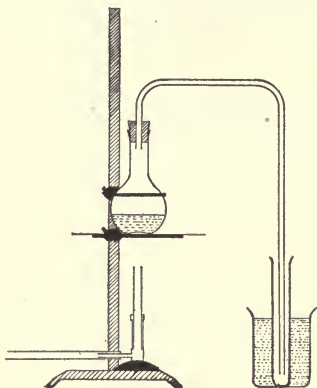


FIG. 96.

The test tube serves as both condenser and receiver. Distill the water until the *distillate* half fills the test tube. Taste the distilled water. Evaporate 5 c.c. of it to dryness in a **clean** evaporating dish. Note if there is a residue, and its amount. For comparison, evaporate 5 c.c. of hydrant water to dryness, and give the result. Define *distillation*.

b. Boiling Point of Water. Support a flask securely (use clamp or extra ring) on the wire gauze of a ring stand, fill it one third with distilled water, and boil the water. Get the temperature of the boiling water by immersing the bulb of the thermometer in it. Do not read the temperature until it is constant. The bulb must be **completely** immersed. Now wipe the bulb of the thermometer **dry**, and hold the bulb in the escaping steam about 2-3 cm. above the level of the water. Compare the two temperatures, and write them down.

Add more distilled water, if necessary, and one-third of a test tube of **salt**. Boil the salt water, and get its temperature. Also wipe the bulb of the thermometer

perfectly clean and dry, and get the temperature of the escaping steam. Give the results.

c. Melting Point of Ice; a Freezing Mixture. — Into a 50 c.c. beaker put about 30 c.c. of crushed or chipped ice, and stir it with the bulb end of the thermometer. Have the bulb completely immersed. Give the exact reading as shown by your thermometer. Is your thermometer correctly graduated? Now add half a test tube of salt to the crushed ice, and stir the mixture with the thermometer. What is the temperature? Will any other substances give freezing mixtures with ice? Consult text.

EXPERIMENT XII.

CHEMICAL PROPERTIES OF WATER.

Apparatus. — Tongs or forceps, evaporating dish, small wide-mouth collecting bottle, glass square.

Materials. — Sodium, water, blue and red litmus paper, solid sodium hydroxide, quicklime, anhydrous cupric sulphate.

a. Action of Sodium upon Water.

Caution. — Do not handle sodium with **wet hands**, or with **wet forceps**. Do not put sodium into the waste jar. **On no account** leave any sodium on or about your desk or in your locker. Sodium is usually kept under kerosene or ligroin (*cf.* § 525 of text).

What is the appearance of a freshly cut surface of sodium? Is sodium hard or soft? Heavy or light?

Fill your smallest gas-collecting bottle three-fourths full of water, and cover it with a glass square. Draw

aside the cover, drop in a small piece of sodium (not over 8–10 cubic millimeters in volume: size of a wheat grain), and cover it **at once**. Note the action. When the sodium has disappeared, apply a lighted match to the bottle. Result? What gas is formed when sodium reacts with water? Test the solution by rubbing it between the fingers. Result? If you get no decided effect, add a second piece of sodium (**dry hands**) exactly as you did the first, and repeat the test.

Put one piece each of red and blue litmus paper into the solution, and give the results. Compare with Experiment V, §§ *f* and *h*.

b. Add a small piece (same size as sodium used) of sodium hydroxide to 5 c.c. of water. Test the resulting solution with the fingers and with litmus, and compare the effects with those of *a*. Conclusion?

c. Action of Water with Quicklime. — In an evaporating dish treat a lump of quicklime about the size of a small hickory nut, or a large cherry, with water, as long as the water is **completely** absorbed. Do not have an excess of water. Note the result after a few minutes. If no result appears, try the effect of warming the dish slightly. If there is still no result, repeat the experiment with a second lump of quicklime. Use the quicklime prepared from marble, if possible.

How is commercial quicklime made? Of what elements is it composed? What change takes place in slaking it? For what is it used? Consult text for answers.

d. Action of Water with Anhydrous Cupric Sulphate. — Compare the colors of blue vitriol and anhydrous cupric sulphate. To about 1 c.c. of anhydrous cupric sulphate

held in the palm of your hand add one or two drops of water. What two results do you notice? What is the difference, as shown by this experiment, between blue vitriol and cupric sulphate?

EXPERIMENT XIII.

EQUIVALENT WEIGHTS OF MAGNESIUM AND OXYGEN.

Apparatus. — Evaporating dish, watch glass, evaporating apparatus (cf. b), tongs.

Materials. — Magnesium wire or ribbon, dilute nitric acid.

a. The object of this experiment is to determine the number of grams of magnesium that combine with 8 grams of oxygen. The method used is to convert the magnesium into *magnesium nitrate* (cf. § 227 of text), and then to decompose the magnesium nitrate by heat (cf. § 230 of text). The residue is *magnesium oxide*.

In a weighed porcelain evaporating dish weigh out accurately about 0.5 g. of magnesium wire or ribbon. Provide the evaporating dish with a watch glass cover to prevent spattering. Draw this aside slightly, and add dilute nitric acid, a few drops at a time, until the metal has dissolved. Rinse the under side of the watch glass with 10 c.c. of water, collecting the rinsings in the evaporating dish. Remove the watch glass cover when evaporating in b.

b. Evaporate the solution of magnesium nitrate (on a water bath or steam bath if possible; otherwise on a wire gauze) until the residue is syrupy. Be careful to

avoid loss. Further evaporation *over* a flame generally causes spattering; but the heating may be continued safely if the flame is applied from above. Do this as follows:—

Hold the evaporating dish by means of iron or brass tongs grasped in the left hand, and carefully move the dish about, so that the syrupy liquid is spread in a thin layer over the sides of the dish, but not nearer to the edge than *one centimeter*. At the same time hold the Bunsen burner in the right hand, move the flame gently round and round, and direct it upon the contents of the dish. By careful manipulation the magnesium oxide may be obtained as an opaque powder. When the decomposition of the nitrate seems complete, apply the flame from below again. Heat the dish to faint redness for five minutes, cool it, and get its weight. Record your weights as in Experiment VI.

To make sure that the dish is at **constant weight**, heat it carefully once more to redness, let it cool, and weigh it. If there is a loss, repeat the heating. Record the final weight.

c. Get the weight of the oxygen that combined with the magnesium. Then solve the following proportion for x :—

$$\text{Wt. of magnesium} : \text{wt. of oxygen} :: x : 8.$$

Compare the **equivalent** of magnesium thus obtained with that obtained in Experiment X. What is the correct amount? What quantities of hydrogen and of oxygen are equivalent to this weight of magnesium? In what proportion, by weight, are they combined in water?

EXPERIMENT XIV.

SOLUTION AND CRYSTALLIZATION.

Apparatus. — Beaker (50 c.c.), stirring rod.

Materials. — Potash alum, crystallized cupric sulphate (blue vitriol).

a. Put 20 c.c. water into a beaker, add 10 grams powdered alum, and stir two minutes with the stirring rod. Does all the alum dissolve?

b. Heat the beaker carefully on the wire gauze, stirring the contents. Result? Conclusion.

c. Set the beaker with the hot solution in cold water, and stir rapidly until solution cools. Result?

d. Dry the outside of the beaker, and heat again as in *b*. Result? Let the solution stand undisturbed until it is cold. Result? Compare with *c*, and account for the difference.

e. Repeat *a*, *b*, *c*, and *d*, with 20 c.c. water and 15 grams powdered blue vitriol. Results?

EXPERIMENT XV.

PRECIPITATION.

Apparatus. — Test tubes.

Materials. — Solutions of lead nitrate, potassium chromate, barium chloride, and calcium sulphate. Dilute sulphuric acid; alcohol.

a. To 5 c.c. of lead nitrate solution in a test tube add an equal volume of potassium chromate solution. Result? Let tube stand ten to fifteen minutes. Result? The precipitate is *lead chromate*.

b. Repeat *a*, putting together hot barium chloride solution and dilute sulphuric acid. Result after ten to fifteen minutes? The precipitate is *barium sulphate*.

c. To 2 c.c. calcium sulphate solution add an equal volume of alcohol. Result? The precipitate is *calcium sulphate*.

Note.—The insoluble solids formed in *a* and *b* are not the only products of these reactions; the other products are, however, soluble.

EXPERIMENT XVI.

SOLUBILITY OF POTASSIUM CHLORIDE.

Apparatus. — Steam bath, water bath, or wire gauze; evaporating dish, balances.

Materials. — Powdered potassium chloride, distilled water.

a. Make a saturated solution of potassium chloride by shaking 12 grams of the powdered substance in a clean flask with 25 c.c. distilled water at the temperature of the room. Continue shaking every little while for fifteen minutes. Record the temperature of the solution, and then weigh out *accurately* into your evaporating dish about 20 grams of the solution. Now evaporate (see *b*) the water until the residual potassium chloride is perfectly dry, and get its weight. From the results

calculate how much potassium chloride will dissolve in 100 grams of water at the room temperature.

b. If possible, evaporate the solution of *a* on a steam or water bath. If this is impossible, evaporate slowly and carefully on wire gauze, so as to avoid any loss by spattering.

c. Record your results thus:—

	<i>Grams.</i>
Wt. of evaporating dish + water + KCl	=
" " " " alone	=
. . . Wt. of water + KCl	=
Wt. of evaporating dish + KCl	=
" " " " alone	=
. . . Wt. of KCl	=
. . . Wt. of water found : Wt. KCl found :: 100 grams : <i>x</i> .	

EXPERIMENT XVII.

WATER OF CRYSTALLIZATION.

Apparatus. — Test tubes, iron saucer (sand bath).

Materials. — Crystals of zinc sulphate, of potash alum (potassium aluminum sulphate), and of cupric sulphate.

a. Place a few crystals of zinc sulphate in a *dry* test tube, and warm *gently*. Results? Is there evidence of water? Where?

b. Repeat *a*, using a crystal of potash alum. Results?

c. Note the taste of another crystal of potash alum; then heat it *strongly* in an iron dish until no further change occurs. Results?

When the ignited alum is *cold*, taste it. Result? Place it in 5 c.c. water in a test tube, and boil carefully for five minutes. When the water is cool, taste it. Result?

Assuming that heat simply drove off crystal-water from the alum, upon what does the taste of crystalline alum seem to depend?

d. Heat a crystal of copper sulphate (blue vitriol) strongly in an iron dish. Result? When the residue is cold, add a few drops of water to it. Result? Explain.

EXPERIMENT XVIII.

EFFLORESCENCE AND DELIQUESCENT.

Apparatus. — Evaporating dish, beaker, watch glass.

Materials. — Hydrates of sodium carbonate (washing soda) and of sodium sulphate (Glauber's salt), solid potassium hydroxide, anhydrous calcium chloride.

a. Expose a bright crystal of washing soda to the air for at least twenty-four hours. Result?

b. Carefully weigh your evaporating dish, and then weigh into it *accurately* about 5 g. of bright crystals of Glauber's salt (hydrate of sodium sulphate). Leave the dish uncovered for at least twenty-four hours, and weigh dish and contents. Result? Continue weighing at intervals until there is no further loss. Calculate the per cent of loss. What is it that escapes? Record your results systematically, as in Experiment VI.

c. In a small beaker place a piece of potassium hydroxide, and leave it exposed to the air at least an hour. Result?

d. Weigh an evaporating dish or a watch glass carefully, and then weigh into it *accurately* about 5 grams anhydrous calcium chloride. Let stand at least twenty-four hours, and weigh again. Results? Record the weighings as in b. What do these substances absorb from the air?

EXPERIMENT XIX.

PER CENT OF WATER OF CRYSTALLIZATION.

Apparatus. — Evaporating dish, balances, wire gauze, ring stand.

Materials. — Powdered gypsum (*not* plaster of Paris), chemically pure barium chloride (the hydrate).

a. Weigh your evaporating dish (be sure it is clean and dry), and into it weigh *accurately* about 3 grams of finely powdered gypsum. Get the exact weight of the gypsum taken, and record it.

b. Heat the evaporating dish on a clean wire gauze for ten minutes with the hottest Bunsen flame. Then let the dish cool, weigh it, and record the result. Now heat the dish again for five minutes, let it cool, and determine the weight. Continue until you have “constant weight.”

c. Record your results thus:—

		Grams.
Wt. of evaporating dish + gypsum	=	
“ “ “ “ alone	=	
∴ Wt. of gypsum taken	=	
Wt. of evaporating dish + calcium sulphate	=	
“ “ “ “ alone	=	
∴ Weight of water found	=	
∴ Per cent of water in gypsum =		

d. Weigh into the evaporating dish, accurately, about 3 grams of pure, powdered barium chloride. Place the evaporating dish on a wire gauze about 4 inches (1 dm.) above the top of a Bunsen flame. Heat the dish for ten minutes, then let it cool, and weigh it. Heat it again, to constant weight. Record the results as in c, and calculate the per cent of water driven off.

EXPERIMENT XX.

DEFINITE PROPORTIONS.

Apparatus. — Evaporating dishes, beaker, balances, watch glass.

Materials. — Sodium bicarbonate, dilute hydrochloric acid.

a. Weigh your evaporating dish carefully, and then weigh into it *accurately* about 5 grams of sodium bicarbonate. Transfer the bicarbonate *without loss* to a beaker covered with a watch glass; then add the dilute hydrochloric acid a little at a time. When adding acid draw the watch glass a little to one side; at other times let it cover the beaker.

b. The *effervescence* (foaming) is due to the escape of carbon dioxide gas. When all the solid has dissolved, add a drop or two more of the acid, to be sure no bicarbonate remains; then pour the solution into the weighed evaporating dish. With 5 c.c. water, wash what has splattered on the watch glass into the beaker, and with this water rinse what adheres to the beaker into the evaporating dish. Rinse the beaker with 5 c.c. more water, and add the rinsings to the evaporating dish.

c. Evaporate the solution to *dryness*, on a water bath or a steam bath, if possible; otherwise, on a wire gauze. If you use wire gauze take great care to avoid spattering either the solution or the solid which remains after the water has boiled away. If considerable spattering begins, remove the flame for a moment and let the dish cool; then apply the flame again *gently*. *Keep flame in constant motion at the end of the process.*

When the solid in the dish is perfectly dry, let the dish cool to the temperature of the room. Then weigh it *accurately*. Heat to constant weight.

d. Record your results thus: —

		Grams.
Wt. of evaporating dish + sodium bicarbonate	=	
" " " " alone	=	_____
∴ Wt. of bicarbonate used	=	
Wt. of evaporating dish + sodium chloride	=	
" " " " alone	=	_____
∴ Wt. of sodium chloride formed	=	

Get the simplest ratio between the amount of bicarbonate taken and that of sodium chloride obtained as follows:—

Wt. of bicarbonate : Wt. of sodium chloride :: 1 : x .

Calculate the value of x to two decimal places. $x = ?$

e. Repeat the preceding operations, weighing out *accurately* about 8 grams sodium bicarbonate. If the volume of the solution is too great to go into the evaporating dish *all at once*, evaporate part of the water and then add the remainder of the solution. *Be sure to rinse.*

Calculate the ratio between sodium bicarbonate and sodium chloride as before. Compare the ratios. Conclusion?

EXPERIMENT XXI.

CHLORINE.

Caution. — *Avoid inhaling much chlorine.* If you have inhaled it, smell ammonia cautiously. If the gas gets into the room, sprinkle a few drops of ammonia water upon your table.

Apparatus. — 100 c.c. flask, ring stand, wire gauze, one-holed stopper, two right-angled tubes (one with long arm), rubber connector, collecting bottle, test tubes, perforated cardboard cover.

Materials. — Manganese dioxide (in lumps), concentrated hydrochloric acid, white paper, red cheese cloth, litmus solution, indigo solution, potassium chlorate, ink, printed paper.

a. Support a 100 c.c. flask on a wire gauze in a ring stand. The flask is provided with a one-holed stopper and a delivery tube bent twice at right angles. The double bend is produced by joining two right-angle tubes by means of a rubber connector. The second right-angle tube is turned down; its end should be 2 to 3 cm. above the table.

b. Put into the flask half a test tube of manganese dioxide in small lumps, add 20 c.c. concentrated hydrochloric acid, and attach stopper and delivery tube.

Warm the flask *gently*, and fill a dry bottle, turned mouth up, with the resulting *chlorine* gas. While the bottle is being filled keep it covered with a piece of card-

board; the cardboard has a hole for the delivery tube. You may know when the bottle is full by the rise of chlorine to the top; white paper held behind the bottle will help you.

c. Stopper the bottle when it is full, and fill two dry test tubes with the gas. Then pass the gas for five minutes into 15 c.c. *cold* water in a test tube. This gives *chlorine water*.

When you are through, disconnect the apparatus *at once*, and wash the remaining manganese dioxide twice with water.

d. What is the color of the gas? Apply a lighted match to a test tube of it. Does the gas burn? Support combustion?

e. Put into the bottle of the gas a small piece (2 cm. square) of *dry* red cheese cloth, a *wet* piece of the same, a piece of paper containing print, and a paper with ink marks. Leave ten to fifteen minutes. Results?

f. Put 5 c.c. of the solution of chlorine made in c upon 1 sq. cm. of the colored cloth in a test tube. Upon paper with both print and ink marks on it. Results? What seems to be necessary in order that chlorine may bleach?

g. Into a test tube of the gas pour 5 c.c. cold water, close the mouth of the test tube tightly with the thumb, and shake *vigorously*. Remove thumb under water. Result? Explain.

h. To 1 c.c. dilute litmus solution, add chlorine water until you get a decided change. Explain result. Repeat, using indigo solution instead of litmus. Result?

i. An easy way to make a solution of chlorine is to treat about 1 gram of potassium chlorate with 5 c.c.

concentrated hydrochloric acid. If action is *slow*, warm *gently*. When the effervescence is rapid, add 10 c.c. cold water.

EXPERIMENT XXII.

HYDROGEN CHLORIDE.

Apparatus. — Same as in Experiment XXI.

Materials. — Sodium chloride, concentrated sulphuric acid, red and blue litmus paper, iron filings, silver nitrate solution, ammonium hydroxide solution, dilute hydrochloric acid, sodium chloride solution, calcium chloride solution.

a. Into a 100 c.c. flask with stopper and delivery tube as in Experiment XXI, put 5 to 7 c.c. water, and add *carefully* 20 c.c. concentrated sulphuric acid. Result?

Caution. — In diluting sulphuric acid always pour the acid *into the water*.

b. Cool the diluted acid by holding the flask in a stream of running water. When the acid is cold, put into it about 15 grams sodium chloride.

c. Attach the stopper and the delivery tube, and place the flask on the wire gauze of a ring stand. Warm carefully with a small flame, and fill a *dry* bottle with the gas, — it is *hydrogen chloride*, — as in Experiment XXI, b.

You may know that the bottle is full when white fumes escape about the cardboard which covers the collecting bottle.

Fill, also, a dry test tube, and stopper both vessels.

d. Test the gas at the end of the delivery tube with strips of moistened red and blue litmus paper. Results?

Blow your breath against the stream of gas. Result? Explain.

e. Now let the end of the delivery tube come *just to the surface* of 5 c.c. water in a test tube. Note the appearance of the water below the delivery tube. While the gas is coming off regularly, raise the test tube so that the end of the delivery tube is about 2 cm. below the water level. Do gas bubbles pass *through* the water? Why? Lower the test tube again until the delivery tube is at the surface, and let the gas run into the water five minutes. Is there any change in temperature?

Finally remove the delivery tube from the water and extinguish the flame. Save the liquid.

Lower the wire gauze so as to let the flask cool out of contact with the gauze.

f. Open the test tube of gas under water. Result? Explain.

g. Hold a burning match in the bottle of gas. Does the gas burn? Does it support combustion?

h. Test the liquid obtained in e with red and blue litmus. Compare results with those given by the gas. Add a drop of the liquid to 2 c.c. water, and taste a drop held on a stirring rod. Result?

i. Pour some of the liquid of e upon 1 c.c. iron filings in a test tube. Result? Does the gas burn?

The equation is: $\text{Fe} + 2\text{HCl} \longrightarrow \text{FeCl}_2 + \text{H}_2$

j. Add a few drops of the liquid of e to 1 c.c. silver nitrate solution in a test tube. Result? The white precipitate is *silver chloride*, AgCl.

The equation is:



To the precipitate add an excess of ammonium hydroxide solution, close the test tube with the thumb, and shake vigorously. Result?

k. Repeat *j*, using sodium chloride solution in place of hydrochloric acid. Result? Write the equation.

l. Repeat *j* again with calcium chloride solution in place of the acid. Results? Conclusion? Equation?

m. Note the white solid which separates when the flask becomes cool. It is chiefly sodium hydrogen sulphate, NaHSO_4 . Write the equation.

EXPERIMENT XXIII.

WEIGHT OF A LITER OF OXYGEN.

Apparatus. — Hard-glass test tube, one-liter bottle, bent glass tubes, pinch-clamp, graduated cylinder, balances, large beaker or bottle.

Materials. — Powdered, chemically pure potassium chlorate, dried at 120°C . Water at room temperature.

a. Set up the apparatus shown in Fig. 97. *A* is a hard-glass test tube that can be slipped tightly over a rubber stopper. *B* is a liter bottle fitted with a two-hole rubber stopper. The longer tube reaches *almost* to the bottom of *B*, and is connected by a rubber tube with *D*, which reaches to the bottom of *C*. The rubber tube

may be closed by the pinch-clamp *F*. Almost fill the bottle *B* with water having the temperature of the room and then fill the tubes *B*, *F*, *D*, with water by sucking at the lower end of *D*, *A* being removed. Then close the pinch-clamp.

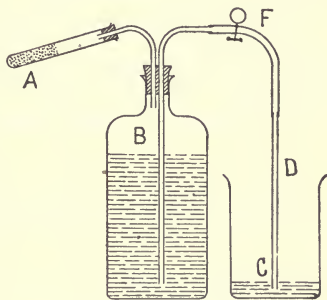


FIG. 97.

b. Into the test tube *A* put about 5 c.c. of powdered, chemically pure potassium chlorate; it must have been dried at 120°C . for at least an hour. Get the weight of test tube and chlorate *accurately* on the balances, and record it.

c. See that the stopper is pressed securely into the mouth of *B*, and then slip *A* carefully, but tightly, over its stopper. Now put about 50 c.c. water into *C*, raise *C* so that the water in *B* and *C* are at the same level, open the pinch-clamp one minute, and then close it. Then put *C* down on the table. Take *D* carefully out of *C* and get the volume of the water in *C*; then pour the water back into *C*, and put *D* in place. Now open the pinch-clamp, and hang it upon the glass tube to the left of *F*. Do not allow the lower end of *D* to get above the surface of the water in *C*. Why?

d. Heat the chlorate in *A* *gently*, beginning with a moving flame. The evolved gas forces water from *B* into *C*. When *C* is about full, stop heating, and let *A* cool to room temperature. Then raise *B* or *C*, as necessary, to make the water levels in both the same (be sure to keep the lower end of *D* under water), close the rubber

tube with the pinch-clamp, and get the volume of the water in *C*. This, *minus* the original volume, equals the volume of gas collected in *B*.

Find the barometric height, correct it for the pressure of water vapor (see Appendix), and find the temperature of the gas. Finally, weigh *A*.

e. Record your results thus: —

		Grams.
Wt. of test tube + contents at first	=	
Wt. of test tube + contents afterward	=	
∴ Wt. of oxygen	=	
Vol. of oxygen	=	c.c.
Temperature of oxygen	=	° C.
Barometer height (corrected)	=	mm.
∴ Volume of O at 0° C. and 760 mm.	=	c.c.
∴ Wt. of 1 l. O at 0° C. and 760 mm.	=	g.

EXPERIMENT XXIV.

PROPERTIES OF ACIDS.

Apparatus. — Stirring rod, test tubes or beakers.

Materials. — Nitric, sulphuric, and tartaric acids; litmus paper, phenolphthalein solution.

a. Make a very dilute solution of sulphuric acid by adding *three drops* of the concentrated acid to 10 c.c. water in a *clean* vessel. By means of a *clean* stirring rod bring a drop of this solution to the tongue. What is its taste?

Note. — Whenever you taste a substance in this way always

be sure that it is *greatly diluted*. Keep it in the mouth long enough to determine the taste *definitely*; then reject it.

b. By means of the stirring rod — it must be washed after every test — bring a drop of the dilute acid of *a* upon red and blue litmus papers. Results? A solution which turns neutral or blue litmus *red* is said to have an *acid reaction*. To the dilute acid add a drop of *phenolphthalein* solution. Result?

Note. — Litmus paper should not be wasted. One piece will do for many tests, if you use only a *drop* of the liquid each time. A new place on the litmus paper must, of course, be used at every trial. *To avoid mistakes* by reason of substances which may have spilled upon the table, lay the litmus paper upon the bottom of a *clean, inverted* beaker.

c. Try the same experiments as in *a* and *b* with nitric acid. Results? With tartaric acid. In the case of the tartaric acid use the solution obtained by heating a small crystal with 5 c.c. water. Results?

d. From Experiment XXII, *i*, tell what happens when iron is treated with hydrochloric acid. Gaseous product? Write the equation here.

From Experiment VIII tell what products are formed from zinc and dilute sulphuric acid. Write the equation.

From Experiment X tell what products are formed from magnesium and dilute sulphuric acid. If magnesium sulphate is MgSO_4 , write the equation.

e. What seems to be the common gaseous product formed when metals act upon acids?

EXPERIMENT XXV.

PROPERTIES OF BASES.

Apparatus. — Same as in Experiment XXIV.

Materials. — Solid sodium hydroxide, potassium hydroxide, and calcium hydroxide, ammonium hydroxide solution, litmus, filter paper, phenolphthalein solution.

a. Dissolve a small piece of sodium hydroxide, NaOH , in 10 c.c. water. Rub a drop of the solution between the fingers. Result? Dilute 3 drops of this with 5 c.c. water and taste the solution, using a stirring rod. Result? Find its effect upon blue and red litmus as in Experiment XXIV, *b.* Result? Add a drop of phenolphthalein to it. Result? A solution which turns neutral or red litmus blue has an *alkaline reaction*.

b. Repeat *a*, using potassium hydroxide instead of sodium hydroxide. Results?

c. Add 2 drops of ammonium hydroxide solution, NH_4OH , to 5 c.c. water. Note taste of dilute solution and its action on blue and red litmus and phenolphthalein.

d. Treat about 1 gram calcium hydroxide, $\text{Ca}(\text{OH})_2$, or calcium oxide, CaO , with 10 c.c. water, stir one minute, and then filter. Examine the solution — it is called *lime-water* — as to taste, feel, and action upon blue and red litmus and phenolphthalein.

EXPERIMENT XXVI.

PROPERTIES OF SALTS.

Apparatus. — Same as in Experiment XXIV.

Materials. — Sodium chloride, ammonium nitrate, potassium sulphate, sodium acetate, sodium carbonate, disodium hydrogen phosphate, phenolphthalein solution.

a. Treat about one cubic centimeter of sodium chloride, NaCl, in a test tube with 5 c.c. water. Test the solution with blue and red litmus as in Experiment XXIV, *a* and *b*. Results? Test it with phenolphthalein. Result?

b. Repeat *a* with ammonium nitrate, NH_4NO_3 ; with potassium sulphate, K_2SO_4 ; with sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$. Results?

c. Repeat *a*, using sodium carbonate, Na_2CO_3 ; disodium hydrogen phosphate, Na_2HPO_4 .

d. Arrange in a table the reactions of the substances you have examined with litmus in Experiments XXII, XXIV, XXV, and XXVI, thus: —

FORMULA OF SUBSTANCE.	ACTION UPON RED LITMUS.	ACTION UPON BLUE LITMUS.
HCl etc.		
NaOH etc.		
NaCl etc.		

What element is found in every acid? What two elements are found in every basic hydroxide? What element is not present, usually, in the *salts*, i. e., the substances studied in this experiment?

EXPERIMENT XXVII.

NEUTRALIZATION.

Apparatus. — Evaporating dish, stirring rod, wire gauze, ring stand.

Materials. — Litmus solution and paper, sodium hydroxide solution, dilute hydrochloric and nitric acids.

a. To 5 c.c. ten per cent sodium hydroxide solution in an evaporating dish add 1 c.c. litmus solution; then add slowly dilute hydrochloric acid until the litmus changes color.

During the addition of acid, stir constantly with a glass stirring rod. If you get too much acid, add sodium hydroxide by means of the stirring rod until the color just becomes blue again; then add a *small* drop of *very dilute* hydrochloric acid. With care you can get the litmus to assume a color intermediate between the red and the blue, viz.: a decided *lavender*. This is the color of *neutral* litmus, and its formation shows that the basic properties of the sodium hydroxide solution have been *neutralized* by the hydrochloric acid.

b. Put a drop of the solution upon red litmus, as in Experiment XXIV, *b*; upon blue litmus. Result?

c. Evaporate the solution carefully. At the end, when

the water is nearly all off and spattering begins, heat with a small flame *in constant motion*.

d. Examine the product obtained in *c*, noting its taste, solubility in water, and the reaction of the solution with litmus. Results?

The substance obtained is *sodium chloride*, or common salt. Complete the equation, $\text{NaOH} + \text{HCl} \longrightarrow ? + ?$

e. Repeat *a*, *b*, *c*, and *d*, using dilute nitric acid instead of hydrochloric acid. Results?

If the product has the formula NaNO_3 , complete the equation, —



EXPERIMENT XXVIII.

NORMAL AND ACID SALTS.

Apparatus. — Two evaporating dishes, burette, test tube, rubber band, filter paper.

Materials. — Pure concentrated sulphuric acid, ten per cent potassium hydroxide solution, phenolphthalein.

a. Put a small rubber band *evenly* around a test tube to mark off 5 c.c. (see Experiment I). Do not change the position of the rubber during the experiment.

b. Dilute 15 c.c. pure concentrated sulphuric acid by pouring it into 35 c.c. water; stir the mixture with a glass rod, and cool it as in Experiment XXII, *b*.

Hold your marked test tube vertically and pour in the dilute acid up to the mark. See that the *upper* edge of the rubber is just at the *lower* level of the *meniscus*, i. e.,

the curved surface of the liquid. Pour the 5 c.c. of acid into an evaporating dish, rinse the test tube with 5 c.c. of water, and add the rinsings to the acid in the dish.

Note what part of your evaporating dish is occupied by the resulting 10 c.c. of liquid, for comparison in *e* of this experiment. Add to the evaporating dish 3 drops of phenolphthalein solution.

c. Fill a burette with ten per cent potassium hydroxide solution. The burette is best fitted with rubber and a glass tip controlled by a pinch-clamp. If a glass stop-cock is used see that it is well lubricated with vaseline. Support the burette in a clamp, put under it a beaker, and let the liquid run out until the part of the burette below the clamp is filled with liquid. Return the liquid which ran out to the burette. Read the level of the liquid *exactly* to tenths of a cubic centimeter, having your eye in the same horizontal plane with the bottom of the meniscus. Record this reading.

d. Open the clamp of the burette *carefully*, and let the potassium hydroxide solution fall *drop by drop* into the evaporating dish of dilute acid. Stir constantly. Get the solution exactly neutral, or at any rate have only one drop of alkali in excess.

Read the burette again. How much alkali was used?

e. Evaporate the solution to about 12 c.c., and let it cool thoroughly. Result?

f. Repeat *b*, *c*, and *d* with twice the quantity of dilute acid, *i. e.*, 10 c.c., and exactly as much potassium hydroxide as was used in *d*.

Test solution with litmus. Result? Evaporate the resulting solution to 5 c.c., and let it cool. Result.

g. Dry the solid substance obtained in *e* between filter

papers. What is the general shape of the crystals? Heat one in a dry test tube. Has it crystal water? Treat some of the crystals with 1 to 2 c.c. water in a test tube. Are they *easily* soluble? What is the reaction of the solution to litmus? Its taste?

h. Treat the crystals obtained in *f* as directed in *g*. Results? Are the crystals in the two cases alike?

How many salts does sulphuric acid form with potassium hydroxide, according to this experiment?

EXPERIMENT XXIX.

NORMAL AND ACID SALTS CONTINUED.

Apparatus. — Same as in Experiment XXVIII.

Materials. — Concentrated pure hydrochloric acid, ten per cent potassium hydroxide solution, phenolphthalein.

a. In the marked test tube (see Experiment XXVIII, *a*) measure out 5 c.c. concentrated hydrochloric acid, put this acid into an evaporating dish, and rinse the tube with 5 c.c. of water, as in Experiment XXVIII, *b*. Add phenolphthalein, and neutralize with ten per cent potassium hydroxide from the burette. Note the amount of alkali used.

b. Evaporate the neutral solution to dryness. Finally, heat the evaporating dish until no fumes of any kind come off, and even the *crackling* sound — *decrepitation* — practically ceases.

Let the dish cool thoroughly.

c. Examine the product, noting its solubility in water, the taste of the solution, and its reaction with litmus.

d. Repeat *a*, *b*, and *c*, with the same amount of alkali, but with twice the quantity, *i. e.*, 10 c.c., of hydrochloric acid.

Be sure to evaporate as directed in *b*.

e. Compare results with those obtained in *c*. How many salts do you get hydrochloric acid to form with potassium hydroxide?

EXPERIMENT XXX.

IONIZATION.

Apparatus. — Test tubes, mortar and pestle.

Materials. — Solutions of silver nitrate, potassium chloride, potassium chlorate, sodium hydroxide, and potassium ferrocyanide; solid ferrous sulphate, sodium bicarbonate, and tartaric acid.

a. Double decomposition between two salts. Review Experiment XV, *a*, and write the equation here. In the double decomposition reactions of *acids*, *bases*, *salts*, and *water*, the materials that react may be classified under the following heads:

- | | |
|--------------|------------------|
| 1. Metals, | 3. Acid radical, |
| 2. Hydrogen, | 4. Hydroxyl. |

Classify the materials of the two salts of Experiment XV, *a*, under these heads.

Take 2 c.c. silver nitrate solution in each of two test tubes. To one add a few drops of potassium chloride solution. Write the equation, indicating the precipitate by an arrow ($\downarrow$). Classify the materials that react in this case also. Why is a precipitate formed?

To the other tube of silver nitrate add some pure potassium chlorate solution. Result? Write the *equilibrium equation* ($\rightleftharpoons$) for the reaction. Why is there no precipitate? Of what radical is the chlorine a part?

b. Double decomposition between salts and bases.

Powder about 1 c.c. of ferrous sulphate, FeSO_4 , and shake it with 5 c.c. of water. Pour off the solution, and add to it a few drops of sodium hydroxide solution. Result? If the precipitate has the formula $\text{Fe}(\text{OH})_2$, write the equation. Classify the materials that react in this case.

Treat about 3 c.c. of potassium ferrocyanide solution, $\text{K}_4\text{Fe}(\text{CN})_6$, with a few drops of sodium hydroxide solution. Result? Why is $\text{Fe}(\text{OH})_2$ not precipitated as before? Of what *radical* is the iron a part?

c. Double decomposition between salts and acids.

Review Experiments XV, *b*, XX, *a*, and XXII, *m*, and rewrite the equations here. Use the proper arrows for precipitates or escaping gases. Classify, as in *a*, the materials that react in the case of salts and acids.

Grind together about 1 c.c. each of sodium bicarbonate and tartaric acid in a dry mortar. Is there any evidence of a reaction? Now add water, and account for the difference. Write the equation (*cf.* § 280 of text).

d. Double decomposition between acids and bases.

Review Experiments XXVII to XXIX. Write here the equations involved. Classify the materials of acids and bases that react by double decomposition. What **one substance** (not class) is always formed in neutralization? What materials unite to produce it? What becomes of the other two? For which materials do we **test** with *indicators* like litmus and phenolphthalein?

EXPERIMENT XXXI.

HYDROLYSIS AND REPLACEMENT.

Materials. — Litmus paper, antimony chloride, bismuth nitrate, iron nails (brads), copper turnings, and zinc (strips or granulated); concentrated hydrochloric and nitric acids; solutions of aluminum chloride, cupric sulphate, mercurous nitrate, and silver nitrate.

a. To a small amount (half a c.c.) of antimony chloride, SbCl_3 , add 5 c.c. water, and shake the two together. Result? If the product first formed is *antimony*
OH
dihydroxychloride, SbOH , write the equation.
Cl

b. To the precipitate add concentrated hydrochloric acid, a drop at a time, warming after each drop. Result? If the solution contains antimony chloride, SbCl_3 , write the equation.

c. Add the solution obtained in *b* to 50 c.c. water. Result? Add concentrated hydrochloric acid again. Result?

d. Compare the equations of *a* and *b*. Write one of them, using, instead of the equality sign, the *double arrow* $\rightleftharpoons$. In which direction does the reaction go chiefly when an excess of water is used? When an excess of acid is used?

e. Repeat the experiment with *bismuth nitrate*, $\text{Bi}(\text{NO}_3)_3$, and water, and use concentrated nitric acid instead of hydrochloric acid. Write the equation.

f. Recall Experiment XXVI for the reaction of *salt* with litmus. For the reaction of sodium carbonate. Try the action of aluminum chloride solution with red and blue litmus paper. Complete the equations, —



For which of these three reactions do you get no evidence from the behavior with litmus? Of what reaction is hydrolysis the reverse? Why is it so incomplete as compared with its reverse?

g. **Replacement.** To 5 c.c. cupric sulphate solution in a test tube add several small iron nails (brads) and let stand over night. Result? What change has occurred in the color of the solution. What is the precipitate? Write the equation.

Repeat, using *mercurous nitrate* (HgNO_3) solution with copper turnings. Equation?

Repeat again, with strips of zinc, or granulated zinc, and *silver nitrate* solution. Result and equation? Compare the results with the action of a metal on an acid, as in Experiment VIII.

EXPERIMENT XXXII.

NITROGEN.

Apparatus. — 100 c.c. flask, wire gauze, ring stand, clamp, stopper, delivery tube, pneumatic trough, collecting bottle.

Materials. — Sodium nitrite, NaNO_2 ; ammonium chloride, NH_4Cl .

a. Support a flask by means of a clamp about its neck, and place under it the wire gauze. Put into the flask 5 c.c. *powdered* sodium nitrite, 5 c.c. ammonium chloride, and 50 c.c. water.

Attach the stopper and delivery tube; the delivery tube extends to a pneumatic trough containing water and an inverted collecting bottle full of water.

b. Have ready your evaporating dish full of *cold* water. Heat the flask *gently* until a regular but not too rapid stream of gas escapes. If at any time during the heating the evolution of gas (nitrogen) becomes *violent*, remove the delivery tube from the water, take away the flame and wire gauze, and bring the evaporating dish of cold water up over the bottom of the flask. Let two test tubes of gas escape (why?); then fill the bottle with it.

c. Determine the odor and color of the gas, also its relation to combustion.

Write the equations for the *stages* of the reaction; also the complete equation.

EXPERIMENT XXXIII.

AMMONIA.

Apparatus. — Mortar and pestle, stirring rod, test tubes, 100 c.c. flask, stopper, two right-angle tubes, collecting bottles, gauze.

Materials. — Glue, quicklime, litmus, hydrochloric acid, ammonium chloride, ammonium nitrate, ammonium sulphate, sodium hydroxide solution, potassium hydroxide solution.

a. Mix in a mortar about one half gram glue and 2 grams quicklime, and heat the mixture in a test tube. Hold in the mouth of the tube, without touching the tube, a piece of moist blue litmus paper. Red litmus paper. A glass rod which has been dipped into concentrated hydrochloric acid. Results? Note odor. What is it?

b. To about one half gram ammonium chloride in a test tube add 2 c.c. ten per cent sodium hydroxide solution, and warm gently. Odor? Effect of gas on litmus? On a rod wet with concentrated hydrochloric acid?

c. Repeat *b*, using ammonium nitrate and sodium hydroxide solution. Results? Use ammonium sulphate and ten per cent potassium hydroxide solution. Results? The gas formed in the above cases is ammonia, NH_3 .

d. In a 100 c.c. flask mix 10 grams powdered ammonium chloride and 20 grams powdered quicklime. Odor? Support the flask on wire gauze and attach the stopper and a delivery tube bent twice at right angles (see Experiment XXI, *a*). Have the second right-angled tube turned *upward*. On a small ring fastened high up on the ring stand, lay a piece of cardboard with a small hole in it; through the hole pass the delivery tube, and invert over the delivery tube the *dry* receiver (bottle) intended to collect the ammonia.

e. Heat *very gently*. When the bottle is full of gas, — test this by waving air from the bottle toward the nose, — cover it and place it mouth down upon the table. Fill three bottles with the gas. Now turn the end of the delivery tube down, so that it just touches the surface of 10 c.c. water in a test tube.

After a minute raise the test tube *carefully* about 2 cm. Do the bubbles of ammonia rise to the surface of the water? Why? Lower the test tube again until the delivery tube just touches the water, and continue heating the flask gently three minutes. Remove the test tube; and *then* extinguish the flame. Let the flask cool not in contact with the wire gauze or any conductor. Why?

f. Did you notice any change in the temperature of the water of the test tube? Explain. Save this liquid.

g. From the method of collecting the gas compare its specific gravity with that of air. Is there any evidence of water in the generating flask?

h. Test the gas in the first receiver with litmus paper — keep mouth of receiver down. Test relation of this gas to combustion. Results?

Thrust up into the receiver a glass rod which has been dipped in concentrated nitric acid. Results? The smoke is ammonium nitrate, NH_4NO_3 . Write the equation.

i. Place the second bottle mouth downward in a pan of water. Result? Explain.

j. Warm the bottom and sides of a clean, dry bottle (having a mouth of the same size as that of the third bottle of ammonia) by moving it *quickly* to and fro in the Bunsen flame; put into it five drops concentrated hydrochloric acid, and place over the bottle of hydrochloric acid gas thus obtained, the bottle of ammonia. Hold the mouths of the bottles firmly together and reverse their positions, so that the ammonia bottle is below the other. Results? What is the product?

k. Examine the solution of ammonia made in e.

What effect has it upon litmus? Hold a piece of moist red litmus about 2 cm. above the solution. Result? Explain.

Put 5 c.c. of the solution into a beaker, note the odor, and let beaker stand for twenty-four hours. Is the odor as strong as before? Inference?

l. Put about 5 c.c. of the ammonia solution of *e* into an evaporating dish, and boil it gently for five minutes. Compare odor after boiling with that of some of the original solution.

m. Heat a small amount of ammonium chloride for some time on a piece of porcelain or on platinum. Result?

n. Write the equations for the reactions which took place in *b*, *c*, *d*, and *e*, as double decomposition equations; then show the dissociation of ammonium hydroxide.

EXPERIMENT XXXIV.

NITRIC ACID.

Apparatus. — 100 c.c. flask, cork stopper, delivery tube (in one piece), test tube, beaker, wire gauze, ring stand.

Materials. — Potassium nitrate, concentrated sulphuric and nitric acids, white silk thread, indigo solution, ferrous ammonium sulphate or ferrous sulphate, and copper nitrate.

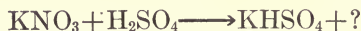
a. Use apparatus of Experiment XI, Fig. 96. Into the flask put 5 g. potassium nitrate and 10 c.c. concentrated sulphuric acid. Attach the stopper and the delivery tube. The delivery tube must be *in one piece without rubber connections*. Put the end of the delivery tube

into a test tube resting in a beaker of cold water. The test tube will serve as a *condenser*.

b. Warm the flask *gradually* over the wire gauze. Result? Color of fumes? Keep the end of the delivery tube out of the liquid which condenses in the test tube.

When no more liquid distills over, remove the delivery tube. Only then remove the flame.

The liquid collected is *nitric acid*. Complete the equation,



What is the color of the acid?

c. Let the flask cool thoroughly. Result? Name the crystalline product. Finally, add water and pour the resulting solution into the sink.

d. Add 1 c.c. of the nitric acid you have made to 1 c.c. of water, and test the action of a drop (use the glass rod) upon litmus. Result?

Into your diluted acid put a piece of white woolen yarn, and warm gently. Remove the yarn. How has it *changed*?

To 1 c.c. of your dilute acid add a few drops of indigo solution. Result?

e. What color does your undiluted acid give to the skin? Will ammonium hydroxide remove the stain?

f. Treat about 2 c.c. of ferrous ammonium sulphate or of ferrous sulphate in a test tube with 15 c.c. water and shake vigorously. Take 5 c.c. of *this solution* in a test tube, add two drops of dilute nitric acid, incline the tube at an angle of about forty-five degrees, and pour about 3 c.c. concentrated sulphuric acid down the side of

the tube. Describe what takes place where the concentrated acid, which is below, meets the solution.

g. Repeat *f*, using a solution of *potassium nitrate* instead of nitric acid. Result? Repeat again with *cupric nitrate* instead of the acid. Result?

h. If the test just tried is a general one for *all nitrates*, how would you proceed to test a solution for the presence of a nitrate or nitric acid?

EXPERIMENT XXXV.

NITRITES.

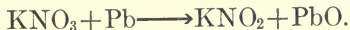
Apparatus. — Iron dish, stout iron wire, beaker, test tubes.

Materials. — Potassium nitrate, lead, filter paper, dilute sulphuric acid.

a. Melt together in a shallow iron dish 10 grams potassium nitrate, KNO_3 , with about 20 grams of lead. Keep the mixture at red heat, and stir twenty minutes with a stout iron wire or a nail held in iron tongs.

b. When the mass is cool add 20 c.c. water, heat to boiling for a few minutes, take out the unused lead, and then filter.

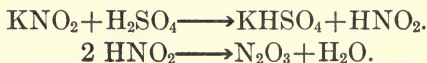
The residue on the filter is lead oxide, PbO . Its color? The filtrate contains potassium *nitrite*, KNO_2 , and unchanged nitrate. The reaction is a *reduction* of potassium nitrate by lead, as is shown in the equation,



c. Treat the solution of potassium nitrite from *b* with dilute sulphuric acid. Result? Treat some potas-

sium nitrate solution in a test tube with dilute sulphuric acid, and compare results.

d. The brown gas is nitrogen trioxide, N_2O_3 , formed as shown by the equations,



EXPERIMENT XXXVI.

NITROGEN TETROXIDE.

Apparatus. — Test tubes, doubly bent delivery tube.

Material. — Powdered lead nitrate, $Pb(NO_3)_2$.

a. Heat 5 grams powdered lead nitrate carefully in a test tube (use a holder), keeping the tube *in constant motion*. Result?

When the tube is full of gas, attach a stopper and a delivery tube with its longer arm *turned down*. Fill a dry test tube with the evolved gas by displacement of air.

b. Invert the test tube of gas in a beaker of water, and leave it a few minutes. Result? Test the residual gas with a pine splinter having a spark on the end of it. Result?

c. The brown gas is *nitrogen dioxide*, NO_2 , mixed with *nitrogen tetroxide*, N_2O_4 .

The equation is,



d. The lead oxide in the test tube may nearly all be

removed by adding to the cold tube dilute nitric acid and heating *carefully*.

EXPERIMENT XXXVII.

NITRIC OXIDE.

Apparatus. — Generating bottle (250 c.c.), two stoppers (one two-holed and one one-holed), funnel tube, delivery tubes, pneumatic trough, wide-mouth collecting bottles, cardboard or glass covers.

Materials. — Copper (granulated or turnings), nitric acid, ferrous sulphate, splinter of pine, red phosphorus.

a. Into a generating bottle (250 c.c.) put enough granulated copper to cover the bottom. Attach stopper containing funnel tube and delivery tube. Add through the funnel tube enough dilute nitric acid to immerse the lower end of the tube, and then concentrated acid, as necessary, to give brisk action. The gas produced is *nitric oxide*, NO. *If the acid is too concentrated, considerable nitrogen tetroxide is produced.*

b. Fill a bottle over water with the gas, and expose it to the air. Result? From the result tell why the gas in the generating flask was originally brown.

c. Pass the gas about three minutes into 10 c.c. concentrated ferrous sulphate solution in a test tube. Result? Save the solution for g.

d. Collect a second and a third bottle full of the gas over water. Cover one of the bottles, remove it from the water, turn it mouth upward, and put into it a lighted splinter. Result?

e. Repeat *d* with the last bottle of the gas, using a deflagrating spoon containing *briskly burning red phosphorus*, instead of the splinter. Compare results. Is nitric oxide a supporter of combustion, or not?

f. Attach to the test tube of solution from *c* a one-holed stopper and a delivery tube. Warm gently and collect the evolved gas over water in a test tube. Expose the gas to the air. Result? Conclusion?

The brown liquid obtained in *c* contains a compound of ferrous sulphate and nitric oxide ($\text{FeSO}_4\cdot\text{NO}$).

See Experiment XXXIV, *f*, where the formation of a brown ring of this compound was used as a test for nitric acid and the nitrates.

g. Pour 25 c.c. of the solution (its color?) left in the generating flask into a beaker, add any unused copper, and let the beaker stand (in a gas chamber if possible) until all action ceases. There should be an *excess* of copper. Pour the liquid into an evaporating dish, and evaporate on a wire gauze to about 10 c.c. Dip into the liquid a glass rod, and see if the liquid which sticks to the rod will solidify on cooling. If so, let the dish cool; if not, evaporate off about 2 c.c. more, and try again. Result?

The substance obtained is *cupric nitrate*, $\text{Cu}(\text{NO}_3)_2$.

Write the *partial* and *complete* equations.

EXPERIMENT XXXVIII.

NITROUS OXIDE.

Apparatus. — Test tubes, stopper, delivery tube, pneumatic trough, clamp, ring stand, collecting bottle.

Materials. — Ammonium nitrate, pine splinter.

a. Into a test tube provided with stopper and delivery tube put about 10 grams ammonium nitrate, and fasten the test tube by a clamp to the ring stand. The test tube should be inclined at an angle of about forty-five degrees.

Invert a bottle of water (best *warm*) in the pneumatic trough, but do not put the delivery tube into the water until *c*.

b. Heat the test tube *gently* with a moving flame. Result? Warm more. Result?

When a steady stream of gas is evolved, hold over the end of the delivery tube a cold and dry beaker. What collects in it?

c. Now put the end of the delivery tube into the pneumatic trough, and fill the collecting bottle with the gas. The gas is *nitrous oxide*, N_2O . Write the equation.

Set the bottle of gas mouth upward and covered upon the table, and then fill a test tube with the gas.

Note. — *Be sure to take the delivery tube out of the water before you remove the flame.*

d. To the test tube of gas add 5 c.c. *cold* water, close the tube tightly with the thumb, and shake vigorously. Open the tube under water. Result?

e. What is the odor of the gas in the bottle? Insert into it a pine splinter with a glowing tip. Result?

What gas resembles nitrous oxide in its *vigorous* support of combustion?

EXPERIMENT XXXIX.

PHYSICAL PROPERTIES OF SULPHUR.

Apparatus. — Test tubes, filter, funnel, evaporating dish, beaker.

Materials. — Powdered roll sulphur, carbon disulphide.

a. Test the solubility of sulphur as follows: In a test tube shake 1 c.c. powdered roll sulphur with 5 c.c. water; filter, and evaporate the filtrate in an evaporating dish. Result? Conclusion?

What is the odor of sulphur? Its taste?

b. Treat *not more than* 1 c.c. powdered sulphur in a test tube with 5 c.c. carbon disulphide.

Caution. — Carbon disulphide is *inflammable*. Do not bring it near a flame.

Close the test tube with the thumb, and shake it thoroughly. Result? Pour the contents of the tube into a *small* beaker, and set this aside in a gas chamber (*not in your cupboard*) until the carbon disulphide evaporates. Result? What is the shape of the larger crystals?

c. Fill a test tube one-third full of sulphur, hold it inclined at an angle of about forty-five degrees, and heat it carefully. Note the changes through which the sulphur passes as you raise its temperature.

What is the color of the liquid formed by melting the sulphur? Is it *viscous* (thick) or *limpid* (thin; easily poured)? Pour a drop of it into water. Color of the product? Is it hard or soft? Sulphur melts at about 114°C .

d. What change does the sulphur undergo when you heat it further? Tilt the test tube to an *almost* horizontal position from time to time *until you find the point at which the liquid cannot be poured*. Then continue heating, and notice that the sulphur becomes limpid again.

Finally, heat the sulphur to boiling. You will know that boiling is taking place when you see the dark brown liquid condensing upon the upper (cooler) parts of the tube. Sulphur boils at 446° to 448°C .

e. Pour the boiling sulphur into a beaker of *cold* water. Result? Color of the product? Is it hard or soft? Elastic or brittle? Keep this for several weeks, noting from day to day any changes that take place.

EXPERIMENT XL.

CHEMICAL PROPERTIES OF SULPHUR.

Apparatus. — Deflagrating spoon, 250 c.c. bottle, cardboard, test tube.

Materials. — Sulphur, blue litmus paper, powdered iron.

a. Put about 1 c.c. powdered sulphur in a deflagrating spoon, heat it in the flame until it burns briskly, and then put the spoon into a bottle of air. Keep the bottle covered with cardboard having a hole in it for the handle of the spoon.

Let the sulphur burn as long as it will. Name the product of the combustion. What is its physical state? Its odor? Try its effect upon *wet* blue and red litmus papers.

b. Mix in a mortar 5.6 grams powdered iron and 3.2 grams powdered sulphur, and put the mixture into a test tube. Heat the lower portion of the tube for a moment in the Bunsen flame. Result? When action begins, withdraw the test tube from the flame. Describe all that takes place.

c. When the product is cool, break the test tube, and remove the solid lump. Describe the product. It is *ferrous sulphide*, FeS .

Write the equation for its formation. Save the solid for Experiment XLI.

EXPERIMENT XLI.

HYDROGEN SULPHIDE.

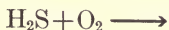
Apparatus. — Test tubes, stopper, and delivery tube.

Materials. — Ferrous sulphide from Experiment XL; dilute sulphuric acid; solutions of cupric sulphate, barium chloride, lead nitrate, cadmium sulphate, sodium hydroxide, and litmus.

Note. — Perform this experiment in a gas chamber, or where there is a *good* draught.

a. Treat the lump of ferrous sulphide made in Experiment XL with dilute sulphuric acid in a test tube. Result? *The gas is hydrogen sulphide*, H_2S . Attach a stopper and delivery tube, and fill a test tube held mouth

upward with the gas. Apply a match to the test tube. Result? Note odor of the burning gas. Result? Complete the equation,



b. Pass the hydrogen sulphide gas from the generating tube into 5 c.c. dilute cupric sulphate (CuSO_4) solution in a test tube. Result? Continue about one minute.

Now see that the delivery tube is clean, and pass the gas three or four minutes into 15 c.c. water in a test tube. Then wash out the generating tube *thoroughly*.

c. Filter the test tube of cupric sulphate into which you have passed hydrogen sulphide. Compare the color of the filtrate with that of the cupric sulphate taken. Conclusion?

The black residue is cupric sulphide, CuS . Write the equation for the action of *hydrogen sulphide* upon *cupric sulphate*.

d. Add a few drops of the hydrogen sulphide solution to 2 c.c. lead nitrate solution, $\text{Pb}(\text{NO}_3)_2$. Result? If the insoluble product is lead sulphide, PbS , write the equation.

Repeat, using *cadmium sulphate* solution in place of *lead nitrate*. Result? If the insoluble product is *cadmium sulphide*, CdS , write the equation.

e. Test the reaction of the hydrogen sulphide solution with red and blue litmus papers. Results? Conclusion?

Add to the remainder of the hydrogen sulphide solution 1 c.c. sodium hydroxide solution. The solution now contains *sodium sulphide*, Na_2S . Write the equation.

f. How would you make ammonium sulphide solution, $(\text{NH}_4)_2\text{S}$? Write the equation.

EXPERIMENT XLII.

SULPHUR DIOXIDE.

Apparatus. — 100 c.c. flask, ring stand, wire gauze, stopper and delivery tube, 2 collecting bottles, test tubes, beaker, evaporating dish.

Materials. — Granulated copper, concentrated sulphuric acid, red flower, red cheese cloth, crystals of cupric sulphate, dilute sulphuric acid, sodium hydroxide solution, litmus paper, concentrated nitric acid, potassium permanganate and potassium dichromate solutions.

a. In a 100 c.c. flask put about 5 grams copper and add 25 c.c. concentrated sulphuric acid. Support the flask in a ring stand, upon wire gauze, and attach a stopper and a doubly bent delivery tube reaching *almost* to the table.

b. Heat the flask *carefully*. When brisk effervescence begins, moderate the heat. Collect 2 bottles of the gas as you did chlorine in Experiment XXI, *b.* Tell when each bottle is full by the odor. Stopper the bottles. Collect, also, a test tube of the gas and put it, mouth down, into a beaker of water. Explain the result.

Wave a little of the escaping gas toward the nose. Odor?

The gas is *sulphur dioxide*, SO_2 .

c. Put the end of the delivery tube *just at the surface* of 10 c.c. water in a test tube. When the gas is coming off freely, raise the test tube about 1 cm. What evidence is there that the gas is dissolving? Lower the test tube to its former position and keep it there five minutes. Then

remove the delivery tube from the water, extinguish the flame, and let the generating flask cool in position, *out of contact with the wire gauze*.

Stopper the test tube containing the solution of the gas, and keep it.

d. Into one bottle of sulphur dioxide gas put a few petals of some red flower, *e. g.*, a carnation; also a small piece of wet, red cloth such as you used with chlorine in Experiment XXI, *e.* Results?

Test the action of sulphur dioxide upon blue litmus paper. Result?

e. To the second bottle of sulphur dioxide add 4 drops of concentrated nitric acid, stopper the bottle, and shake it. Results? Add 5 c.c. water, stopper once more, shake, and pour the liquid into a test tube. Save this for Experiment XLIV, *c.*

f. Note the taste of a drop of the sulphur dioxide solution made in *c.* What is the action of 1 c.c. of it upon 1 c.c. potassium permanganate solution (KMnO_4)? Repeat with potassium dichromate solution instead of potassium permanganate. Result?

Sulphur dioxide solution contains sulphurous acid, H_2SO_3 .

g. Neutralize the remainder of the sulphurous acid in an evaporating dish with 10 per cent sodium hydroxide solution and evaporate to dryness. The resulting substance is *sodium sulphite*, Na_2SO_3 . Describe it.

Complete the equation,

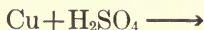


h. Treat the sodium sulphite in a test tube with a little dilute sulphuric acid, and warm. Note the odor.

The sulphite is decomposed by the acid thus: —



i. When the generating flask is *cold*, add to it 25 c.c. water, shake *carefully*, and heat the flask *cautiously* over wire gauze. Filter the resulting liquid. What is the color of the filtrate? Concentrate it to about 15 c.c., and let it cool. Result? Compare the product with blue vitriol, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$. Complete the equation,



EXPERIMENT XLIII.

SULPHURIC ACID.

Apparatus. — File or blue paraffin pencil, test tube, beaker, balances.

Materials. — Concentrated sulphuric acid, sugar, cotton, cloth, paper, splinter.

a. By means of a file or a blue paraffin pencil mark off about 10 c.c. on a clean, dry test tube, set the tube in a clean beaker, and get the weight of both test tube and beaker together. Now fill the tube up to the mark with concentrated sulphuric acid, wipe off any acid adhering to the mouth of the test tube, and get the weight of acid + beaker + test tube.

Return the acid to the bottle, rinse the test tube, and dry it on the outside. Then fill the tube up to the mark with water, and get the weight of water + beaker + test tube.

Record your results thus: —

		Grams.
Wt. of test tube + beaker + sulphuric acid	=	
Wt. of test tube + beaker	=	
. . . Wt. of sulphuric acid taken	=	_____
Wt. of test tube + beaker + water	=	
Wt. of test tube + beaker	=	
. . . Wt. of water taken	=	_____

From the results calculate the specific gravity of your sulphuric acid.

b. Heat *one* drop — no more — of concentrated sulphuric acid in an evaporating dish over wire gauze. Result?

c. Put into a test tube a splinter of wood and add 5 c.c. concentrated sulphuric acid. Let stand fifteen minutes. Try the effect of a drop of concentrated sulphuric acid on paper; upon cotton cloth. Wait for the result if it is not immediate. Results.

d. Into a small beaker put 10 grams sugar and 5 c.c. water, and stir thoroughly. Now add 10 c.c. concentrated sulphuric acid. Results? Describe the product.

EXPERIMENT XLIV.

SULPHATES.

Apparatus. — Test tubes.

Materials. — Concentrated sulphuric acid; solutions of barium chloride, cupric sulphate, sodium sulphate; dilute hydrochloric acid; liquid from Experiment XLII, *e*.

a. To 10 c.c. water in a test tube add 1 c.c. concentrated sulphuric acid. Result? Heat the diluted acid to boiling, and add 5 c.c. barium chloride solution, BaCl_2 . Result?

The precipitated substance is barium sulphate, BaSO_4 . If the other product is hydrochloric acid, write the equation.

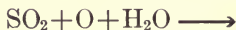
Let the precipitate settle, pour off the *supernatant* liquid, and add 10 c.c. dilute hydrochloric acid to the precipitate. Does the precipitate dissolve?

b. Repeat a, using instead of dilute sulphuric acid 5 c.c. of a solution of cupric sulphate, CuSO_4 . Results? Equation?

Repeat again, using 5 c.c. of sodium sulphate solution, Na_2SO_4 , with 5 c.c. barium chloride solution. Result? Equation?

Note.—*In general*, if a solution gives with barium chloride solution a white precipitate *insoluble in dilute hydrochloric acid*, we are *reasonably* sure that the unknown solution contains sulphuric acid or a *sulphate*.

c. Treat the liquid obtained in Experiment XLII, e, with barium chloride solution. Result? What effect did nitric acid have upon the sulphur dioxide? Complete the equation,



EXPERIMENT XLV.

CARBON.

Apparatus. — Tongs, test tubes, iron dish with a cover, beaker.

Materials. — Charcoal (lumps and powder), graphite (pencil lead), soft coal, hydrogen sulphide solution, litmus solution, brown sugar, animal charcoal.

a. Hold a piece of charcoal in the Bunsen flame (use tongs) and describe its combustion. Repeat with *graphite* (pencil lead) and with soft coal.

b. Fill an *old* test tube one-fourth full of bits of wood, and heat. Results? Bring a burning match to the mouth of the tube. Result? Describe the other products. What is the residue?

c. Hold a piece of wood charcoal under water in a beaker for two minutes. What appears on its surface? Conclusion?

d. Heat powdered wood charcoal or animal charcoal for five minutes in a covered iron dish. Let it cool, and add 2 c.c. of it to 5 c.c. *hydrogen sulphide* solution. Shake thoroughly and filter. Compare odor of filtrate with that of the solution taken. Conclusion?

e. Boil 5 c.c. *litmus* solution two minutes with 2 c.c. of the freshly ignited charcoal, and filter. Result? *Repeat*, using 5 c.c. of a solution of brown sugar with 2 c.c. fresh charcoal. Result?

EXPERIMENT XLVI.

CARBON DIOXIDE, I.

Apparatus. — Generating bottle, stopper with thistle tube and delivery tube, pneumatic trough, beaker, test tubes, and collecting bottles.

Materials. — Marble, hydrochloric acid, litmus, lime-water.

a. Place in a bottle enough marble (a form of *calcium carbonate*, CaCO_3) to cover the bottom, add enough water to close lower end of the thistle tube, insert stopper, and add concentrated hydrochloric acid through the thistle tube. Add more acid when it is needed. Collect the *carbon dioxide* (CO_2) over water, rejecting the first bottle of the gas. See, also, Experiment XX.

b. Put into a bottle of the gas wet litmus paper (red and blue) and a burning match. Results?

c. Pour a bottle of the gas into a beaker of air. Test the gas in the beaker with a burning match. Result? Conclusion as to the specific gravity of the gas?

d. Fill a test tube with the gas by air displacement, add 5 c.c. *cold* water, close tube securely with thumb, shake vigorously, and open under water. Result? Conclusion? .

e. Pass the gas into lime-water, $\text{Ca}(\text{OH})_2$. Result? Let the precipitate settle. It is *calcium carbonate*. Its formation with lime-water is a **test** for carbon dioxide (*cf.* Experiment V, e). Now pass a vigorous stream of the gas into the tube five minutes. Result? Boil the contents of the tube. Result?

EXPERIMENT XLVII.

CARBON DIOXIDE, II.

Apparatus. — Beakers, delivery tube, test tubes.

Materials. — Lime-water, sodium bicarbonate, tartaric acid.

a. Mix 2 c.c. each of *sodium bicarbonate* (NaHCO_3) and *tartaric acid* ($\text{H}_2\text{C}_4\text{H}_4\text{O}_6$) in a mortar. Is a change apparent? Put half of the powder into a test tube, and add water. Result? Identify the gas.

b. Put the remainder of the mixture from *a* in a test tube, add 10 c.c. water, and, as soon as you are able, imprison the gas by holding your thumb upon the mouth of the test tube. Effect upon the effervescence? Now remove your thumb. Effect? Explain.

c. Blow your breath through a delivery tube into 5 c.c. lime-water. Result? Conclusion?

d. Expose 5 c.c. *clear* lime-water to the air for several hours. Result? How does carbon dioxide get into the air (*cf.* Experiment V, *e*)?

EXPERIMENT XLVIII.

REDUCTION BY CARBON. EFFECT OF HEAT ON CARBONATES.

Apparatus. — Ignition tube, delivery tube, rubber connector, test tubes.

Materials. — Lead monoxide, powdered charcoal, lime-water, magnesite.

a. Mix 1 c.c. lead monoxide, PbO , with one-third its volume of powdered charcoal, on *smooth* paper. Into the ignition tube put enough of the mixture to make a layer 1 cm. thick, support the tube almost horizontally, and attach a delivery tube leading into 5 c.c. lime-water. Heat the lead monoxide *persistently* for ten minutes, cool it, and pour it out on the table. Result? What gas was evolved? Write the equation.

b. Fill the ignition tube one-fifth full of chips of *magnesite*, MgCO_3 , and set it up as in *a.* Heat persistently. What gas is evolved? What, then, does the residue contain? Write the equation.

EXPERIMENT XLIX.

FLAMES.

Apparatus. — Bunsen burner and tongs.

Materials. — Candle, piece of porcelain, white paper.

a. Examine carefully the non-luminous flame. Sketch a vertical section of it *as you see it*. Make drawing 4 cm. long.

b. Do the same with a *luminous* Bunsen flame 2 cm. high. Repeat with a candle flame.

c. Press the colorless Bunsen flame for a moment upon paper lying on your table. The paper should not burn up. Result?

Hold a piece of glass tubing about 1 dm. long at an angle of forty-five degrees, with the lower end inside the central part of the non-luminous flame, and apply a lighted

match to the other end. Result? What do these experiments show as to the inner region of the flame?

d. Hold a piece of porcelain (broken evaporating dish) by means of tongs in the luminous flame. Result? What substance is in excess here? Now hold the porcelain in the colorless flame for some time. Result? What is in excess in this flame?

EXPERIMENT L.

BROMINE.

Apparatus. — Beaker, 100 c.c. flask, test tubes.

Materials. — Potassium bromide, powdered manganese dioxide, dilute sulphuric acid, litmus paper, calico, carbon disulphide, chlorine-water, sodium hydroxide.

Caution. — If possible, work in a gas-chamber or hood.

a. Into a flask put an eighth of a test tube of potassium bromide (KBr) crystals, half as much powdered manganese dioxide, and half a test tube of dilute sulphuric acid. Support the flask over wire gauze, and attach the cork stopper and a doubly bent delivery tube reaching into a test tube three-fourths full of cold water. The delivery tube must be without rubber connections. The test tube should rest in a beaker of water (*cf.* Experiment XI).

b. Warm the flask *carefully* until a dark brown distillate passes over. Is it heavier or lighter than water? **Do not inhale the vapor**, and do not get liquid bromine on your hands.

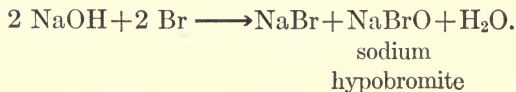
When no more bromine comes over, remove **first** the delivery tube and then the flame. The light-brown solution is "bromine-water."

c. Wave the air from the test tube toward the nose. Odor of bromine? Pour off as much bromine-water as possible without pouring out the bromine, and add more water to the bromine. Pour a few drops of the bromine-water upon litmus paper and upon colored calico. Results?

d. To 3 c.c. water in a test tube add 1 c.c. *carbon disulphide*, close tube with thumb, and shake vigorously. Results? Where is the carbon disulphide? Now add $\frac{1}{4}$ c.c. bromine-water and shake again. Result to the color of the water? To that of the carbon disulphide? *This effect on the carbon disulphide is a test for free bromine.*

e. To 5 c.c. of potassium bromide solution add 1 c.c. carbon disulphide and shake. Result? Now add two or three drops of *chlorine-water* (make as in Experiment XXI, i), close the tube, and shake it as before. Results? Action of chlorine on potassium bromide? Equation?

f. To the liquid bromine saved from c add sodium hydroxide solution, a cubic centimeter at a time, shaking thoroughly. (Do not close the tube with the thumb!) Result? The equation is, —



EXPERIMENT LI.

IODINE AND HYDRIODIC ACID.

Apparatus. — Test tubes, beaker, flask.

Materials. — Potassium iodide, manganese dioxide, sulphuric acid, iodine, carbon disulphide, chlorine- and bromine-water, starch, alcohol, hydrogen sulphide, silver nitrate solution, sodium carbonate, litmus.

a. Powder *potassium iodide* (KI), mix 1 c.c. of it with a c.c. of manganese dioxide, add 2 c.c. water and then 1 c.c. concentrated sulphuric acid. Result? When the action slackens, warm the tube gently, and then let it cool. Describe what you find in the tube. It is *iodine*. Compare its preparation with that of chlorine and bromine.

b. Warm a crystal of iodine (*gently*, not to boiling) with 10 c.c. water for a few seconds. Does the iodine dissolve *readily*? Cool the water and add 3 c.c. of it to 1 c.c. carbon disulphide. Shake the closed tube. Result? *This is a test for free iodine.* Save the iodine solution.

c. Shake 5 c.c. potassium iodide solution with 1 c.c. carbon disulphide. Result? Add a drop of chlorine-water and shake again. Result? What effect has chlorine upon potassium iodide? *Repeat*, using bromine-water instead of chlorine-water. Write both equations.

d. Make a **starch solution** as follows: Mix 2 c.c. powdered starch with 5 c.c. cold water, and pour the emulsion into 30 c.c. boiling water. Boil for a minute or

two, and then cool. To 3 c.c. of the solution add a drop of the iodine solution of *b*, shaking. Result?

To 3 c.c. of the starch solution add one drop of a potassium iodide solution and then one drop of chlorine- or bromine-water. Result?

e. Heat a crystal or two of iodine in a dry, inclined test tube. Result? Let cool. Result? Effect of iodine on the skin? On wood and paper?

f. To the iodine of *e* add 5 c.c. *ethyl alcohol*, C_2H_5OH . In which is iodine more soluble, water or alcohol? An alcoholic solution is often called a *tincture*.

g. To one-half a c.c. of powdered iodine in a flask add 20 c.c. water and then pass in hydrogen sulphide (gas-chamber!) until the iodine disappears. Results? Boil the solution gently two minutes, and filter it. Identify the precipitate by igniting a little on a piece of porcelain. Odor? Test the filtrate with red and blue litmus. Results? Add a drop of it to 1 c.c. silver nitrate solution. Result? Add some to 1 c.c. solid sodium carbonate. Result? What substances are formed from hydrogen sulphide and iodine? Equation?

EXPERIMENT LII.

COMPARISON OF THE HALOGEN ACIDS.

Materials. — Potassium chloride, bromide, and iodide; concentrated sulphuric acid, litmus.

a. Three test tubes have small amounts of potassium chloride, bromide, and iodide, respectively; treat each with a few drops of concentrated sulphuric acid. Re-

sults? Blow your breath across the mouth of each tube. Result? Test the gas of each with blue litmus. Result? Note carefully the odor of each gas. What odors beside that of the acid do you get in the tube of potassium iodide? Heat this tube. Result?

b. Which tube gives a colorless gas? What colors the gas in each of the two other cases? From the amount of coloration, tell which of the three halogen acids is most easily decomposed into its elements. Which least.

EXPERIMENT LIII.

HYDROGEN PEROXIDE.

Materials. — Hydrochloric acid, barium peroxide, starch solution, potassium iodide solution, manganese dioxide, potassium permanganate, ether, potassium dichromate solution, splinter.

a. To 25 c.c. water add 5 c.c. concentrated hydrochloric acid and then 3 grams powdered *barium peroxide*, BaO_2 , a little at a time, stirring. Filter the solution; it should contain *hydrogen peroxide*, H_2O_2 .

b. To 5 c.c. starch solution add a drop of potassium iodide solution, and then a few drops of the hydrogen peroxide solution. Result?

c. To 3 c.c. of the solution of *a* add 3 c.c. ether. Do they mix? Is the ether above or below? Now add *one drop* of potassium dichromate solution. Close tube and shake *gently*. Result?

d. To 5 c.c. of the hydrogen peroxide solution add 1 c.c. powdered manganese dioxide. Result? Test gas with a glowing splinter. Result?

e. To three crystals of potassium permanganate in a test tube add 2 c.c. water and then 5 c.c. of the hydrogen peroxide solution. Result? Test with glowing splinter. Result?

EXPERIMENT LIV.

PHOSPHORUS AND PHOSPHORIC ACID.

Apparatus. — Test tubes, small ignition tube, tongs, evaporating dish, file.

Materials. — Red and yellow phosphorus, carbon disulphide, filter paper, phosphoric acid, ammonium hydroxide, powdered disodium hydrogen phosphate; magnesium sulphate, ammonium chloride, silver nitrate, and calcium chloride solutions.

Caution. — Ordinary, yellow phosphorus must be handled *only with tongs*, **never** with fingers! It must be kept and cut *under water*. No pieces of it must get into your locker; and every dish that has contained phosphorus must be *heated*, so that the phosphorus may be completely burned.

Do not bring carbon disulphide near a flame!

a. Put half a c.c. of red phosphorus into a test tube, and add 3 c.c. carbon disulphide. Result? Filter, and let the carbon disulphide evaporate, without heating, in a hood, or where its vapor will not get near a flame. Result? Was any phosphorus dissolved?

To 3 c.c. carbon disulphide add a piece of *yellow* phosphorus not larger than a *grain of wheat*. Shake carefully a few minutes. Result? Pour the solution, *every drop of it*, upon a piece of filter paper laid flat on a ring of the ring stand. Let the carbon disulphide evaporate with-

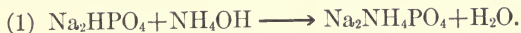
out heating it. Result? Rinse the test tube before putting it away.

b. Into a small ignition tube put a layer of red phosphorus not more than 5 mm. thick, hold tube horizontal (tongs), and *gently* heat end containing the phosphorus. What collects on the cold part of the tube? When the tube is cold, make a file-mark just below the deposit, and break the tube. Rub the deposit with a match stick. Result? Conclusion? *Finally*, heat both tubes red hot, so as to burn up all the phosphorus. Throw the pieces into iron or crockery jars.

c. To 5 c.c. water add 1 c.c. concentrated (ortho) phosphoric acid, *neutralize* in an evaporating dish (use litmus) with ammonia, and add silver nitrate solution. Result? The precipitate is *silver orthophosphate*, Ag_3PO_4 . Write the two equations if the first product is $(\text{NH}_4)_2\text{HPO}_4$.

Dissolve 2 c.c. powdered *disodium hydrogen phosphate* in 10 c.c. water. To half of the solution add calcium chloride solution. Result? The product is *secondary calcium phosphate*, CaHPO_4 . Equation?

d. To 5 c.c. *magnesium sulphate* solution add 1 c.c. ammonia-water and 1 c.c. ammonium chloride solution, and then the disodium hydrogen phosphate solution from c. Result? The product is *magnesium ammonium phosphate*, $\text{NH}_4\text{MgPO}_4 \cdot 6 \text{H}_2\text{O}$.



EXPERIMENT LV.

ARSENIC.

Apparatus. — Small ignition tube, tongs, test tube, beaker.

Materials. — Arsenic trioxide (powdered), charcoal, hydrochloric acid, hydrogen sulphide, ammonium sulphide, sodium hydroxide solution.

a. Into a small ignition tube put powdered *arsenic trioxide*, As_2O_3 , to the depth of 5 mm. Hold the tube *horizontal* and at the *side* of the flame, so as to heat only the end containing the powder. What happens? Now slip into the tube, *almost* to the arsenic trioxide, a piece of charcoal about 2 cm. long. Heat the charcoal red hot (have tube horizontal), and then incline the tube slightly so as to heat the arsenic trioxide while keeping the charcoal red hot. Result? Effect of charcoal upon the oxide? Equation? How does the oxide come into contact with the charcoal? *Sublime* the arsenic obtained.

b. Heat half a c.c. of arsenic trioxide with 8 c.c. dilute hydrochloric acid to gentle boiling. Result? Equation? Pour off from any undissolved material, and pass in hydrogen sulphide for a minute. Result? If visible product is *arsenic trisulphide*, As_2S_3 (its color?), write equation. Let settle, pour off supernatant liquid, and add 5 c.c. *ammonium sulphide* to residue, shaking. Result? (CAUTION. — Do not get *ammonium sulphide* on your hands!) The product now formed is *ammonium sulpharsenite*, $(\text{NH}_4)_3\text{AsS}_3$; it is soluble. Treat solution

with an excess of dilute hydrochloric acid in a beaker. Result?

c. Treat half a c.c. of arsenic trioxide with sodium hydroxide solution. Warm carefully. Result? The solution contains *sodium arsenite*, Na_3AsO_3 . From *b* and *c* would you say arsenic trioxide has *acid*, or *basic*, properties?

EXPERIMENT LVI.

ANTIMONY.

Apparatus. — Mortar and pestle, funnel, ignition tube.

Materials. — Antimony, concentrated nitric and hydrochloric acids, hydrogen sulphide, ammonium sulphide, antimony trioxide, tartar emetic.

a. What is the color of metallic antimony? Is it heavy or light? Powder a small piece, and treat part of it in a test tube with concentrated nitric acid. Results?

b. Treat the remainder of the powdered antimony of *a* with 3 c.c. concentrated hydrochloric acid and 1 c.c. concentrated nitric acid. Warm to start the action, if necessary. The solution contains *antimony chloride*, SbCl_3 . Let action continue for ten minutes; then add 15 c.c. water. Filter, if necessary, and pass in hydrogen sulphide. If there is no action, dilute still more. Result? If the product has the formula Sb_2S_3 , write the equation. Treat the antimony sulphide as you did arsenic trisulphide in Experiment LV, *b*.

c. Dissolve half a c.c. of *tartar emetic* in 5 c.c. water,

add a drop of hydrochloric acid, and pass in hydrogen sulphide. Result? Conclusion?

d. Heat antimony trioxide (Sb_2O_3) in an ignition tube with charcoal, as you did arsenic trioxide. Results?

EXPERIMENT LVII.

BISMUTH.

Apparatus. — Mortar and pestle, beaker, test tubes.

Materials. — Bismuth, concentrated nitric and hydrochloric acids, bismuth nitrate crystals, hydrogen sulphide.

a. What is the color of bismuth? Is the metal heavy or light? Malleable or brittle (test with the pestle)? Treat a bit with concentrated nitric acid. Result? Products?

b. To half a c.c. of bismuth nitrate crystals, $\text{Bi}(\text{NO}_3)_3$, add 5 c.c. water, and shake. Result? If the product has the formula BiONO_3 , write the equation. Now add nitric acid (concentrated) a drop at a time, heating to boiling after each drop. Result? Use the least possible amount of acid.

c. Put half of the solution from *b* into a beaker, and add much water. Result? Compare with first part of *b*.

d. To the remainder of the acidified solution of bismuth nitrate from *b* add hydrogen sulphide. Result? The visible product is *bismuth sulphide*, Bi_2S_3 . Write the equation.

EXPERIMENT LVIII.

BORAX AND BORIC ACID.

Apparatus. — Platinum wire sealed into glass rod, test tubes, beaker.

Materials. — Borax, potassium dichromate, manganese dioxide, hydrochloric acid, and sodium carbonate (solid).

a. Borax Bead. Make a loop 2 mm. in diameter on the end of a platinum wire sealed into a piece of glass tubing. Heat the loop to redness, and dip it into powdered borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$. Heat the adhering borax *just within* the outer edge of the Bunsen flame, at the place *where the flame is widest*. This is the **fusing zone** of the flame. What happens first? Heat until the borax melts to a *transparent* glass. If there is not enough borax to fill the loop, add more, and heat again. This glassy lump is called the **borax bead**.

b. Touch the hot bead to a tiny speck (less than half as large as a pin's head) of *potassium dichromate*, $\text{K}_2\text{Cr}_2\text{O}_7$, and heat at the top of the flame until the dichromate is completely absorbed by the bead. Color? Remove the bead by plunging it while hot into water, and wipe it off the wire.

c. Make a new bead, and touch it to a speck of manganese dioxide. Heat first in the **oxidizing flame** of the burner, *i. e.*, just above the *visible* tip of the flame. Color? Now heat it in the **reducing** region, *i. e.*, just *above* the tip of the *bright blue* interior cone. Heat it there persistently for five minutes, examining it from

time to time. Result? Heat it again in the oxidizing flame. Result?

d. Boric Acid.—Dissolve 5 grams powdered borax in 10 c.c. hot water, and add 10 c.c. concentrated hydrochloric acid. Set aside until next laboratory period. Result? The product is *boric acid*, H_3BO_3 . Filter off the crystals, wash them on the filter with a little cold water, and dry them on fresh filter paper.

e. Dissolve the crystals of boric acid in hot water, and add the solution to a lump of sodium carbonate. Result?

EXPERIMENT LIX.

SODIUM COMPOUNDS.

Apparatus.—Test tubes, stopper and delivery tube, magnifying glass, platinum wire, watch glass or glass slip.

Materials.—Sodium bicarbonate, lime-water, sodium carbonate (solid and in solution), sodium chloride, calcium chloride, barium chloride, sodium nitrate and sulphate, hydrochloric acid.

a. Refer to Experiment XII for the properties of sodium* and its action on water.

b. Heat 2 c.c. powdered sodium bicarbonate carefully in a test tube having a delivery tube that passes into lime-water. Result? Is there any other volatile product? When no more gas is evolved (do not melt the test tube), let the product in the tube cool, and then add 2 c.c. cold water. Note the temperature effect. Compare with this the action of anhydrous sodium carbonate

upon water. What are the products formed by heating sodium bicarbonate? Equation?

c. Heat 2 c.c. sodium chloride with 5 c.c. water in a test tube; filter; and let some of the filtrate evaporate completely on a glass slip or a watch glass. Examine the crystals with a magnifying glass, if possible. Their shape?

d. Dissolve a small piece of *calcium chloride*, CaCl_2 , in 5 c.c. water, and add sodium carbonate solution. Result? Repeat, using *barium chloride* instead of calcium chloride. Result? Write the equations.

e. Dip a platinum wire with a glass holder (*cf.* Experiment LVIII, a) into 5 c.c. concentrated hydrochloric acid in a test tube, and then heat the wire in the Bunsen flame until the flame remains colorless. If necessary, dip the wire more than once. Now wet the clean wire with the acid, dip it into powdered sodium chloride, and heat it. Effect on the flame?

f. Clean the wire and repeat e, using sodium nitrate instead of sodium chloride. Repeat again with sodium sulphate. What color do sodium salts give to the flame?

EXPERIMENT LX.

POTASSIUM COMPOUNDS.

Apparatus. — Watch glass, iron dish, test tubes, beaker or evaporating dish, platinum wire, copper wire.

Materials. — Potassium chloride, sodium nitrate, sulphur, barium chloride solution, potassium hydrogen tartrate, lime-water, dilute sulphuric acid, concentrated hydrochloric acid, potassium nitrate, and potassium sulphate.

a. Heat 8 grams of potassium chloride and 10 grams of sodium nitrate with 20 grams of water until there is complete solution, and boil off half of the water over the wire gauze? Result? Let the precipitate settle and pour the solution into a test tube. Wash the residue with 5 c.c. cold water, and then dissolve it in the smallest possible amount of hot water. Pour a few drops of the solution in a watch glass and set aside. Result? Compare the crystals with those obtained in Experiment LIX, c. Conclusion?

What happens in the test tube containing the original solution? The visible product is *potassium nitrate*, KNO_3 .

b. Mix 3 c.c. powdered potassium nitrate on a clean piece of paper with 1 c.c. powdered sulphur, and pour the mixture, *at arm's length*, upon a hot iron dish (use no wire gauze). Result? Let the product cool, boil it with 10 c.c. water in a test tube, and add to 5 c.c. of it *barium chloride* solution. Result? See Experiment XLIV, b. What is the product of the deflagration of potassium nitrate and sulphur?

c. Heat an iron dish red hot, and pour upon it 3 c.c. powdered *potassium hydrogen tartrate*, $\text{KHC}_4\text{H}_4\text{O}_6$ (cream of tartar). Results? Color of residue? Heat it five minutes longer at red heat, pressing the mass down with a glass rod occasionally. When the dish is cool, treat the residue in a test tube with dilute sulphuric acid. After all evolution of gas ceases, identify the gas by placing in the mouth of the tube a looped copper wire holding a drop of lime-water. What remains undissolved? What substance would you find in plant ashes if the plants contained potassium salts of organic acids?

d. Clean a platinum wire as in Experiment LIX, e; dip it into strong hydrochloric acid, and then into powdered potassium chloride, and heat it in the flame. Result? Repeat, using potassium nitrate instead of the chloride. Use the sulphate. Results? What color do potassium compounds give to the flame?

EXPERIMENT LXI.

AMMONIUM AMALGAM. DISTINCTIONS BETWEEN THE ALKALI METALS.

Materials. — Ammonium chloride, sodium amalgam, sodium and potassium chlorides, tartaric acid, two unknown substances.

a. Dissolve 2 c.c. ammonium chloride in 5 c.c. water, and add a piece of *sodium amalgam* ($\text{Na} + \text{Hg}$). Results? The product is *ammonium amalgam*. Note what happens to it. Odor? Reaction of solution?

Note. — Do not throw away the resulting mercury, but ask what to do with it.

b. Add 5 c.c. water to 3 c.c. powdered potassium chloride and shake thoroughly. Pour off the solution and add to it 5 c.c. of a *concentrated* solution of tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. Make this by shaking 5 c.c. powdered tartaric acid with 15 c.c. water. Wait for result. Result? The product is *potassium hydrogen tartrate*. Equation?

c. Repeat b, using *sodium chloride* in place of potassium chloride. Result? Repeat again, using *ammonium chloride* in place of potassium chloride. Result?

d. From Experiment XXXIII, *b* and *c*, tell what happens when ammonium salts are treated with alkalies. How distinguish between *sodium* salts on the one hand and *ammonium* and *potassium* salts on the other? Between *sodium* salts and *potassium* salts (two ways)?

e. Get from the instructor two unknown substances, and determine if they are salts of sodium, potassium, or ammonium.

EXPERIMENT LXII.

CALCIUM.

Apparatus. — Triangle of iron wire, ring stand, blast-lamp, evaporating dish, platinum wire, and coin.

Materials. — Lumps of marble, lime-water, red litmus paper, old mortar, plaster of Paris, paper, calcium chloride, calcium sulphate, and ammonium carbonate solution.

a. Touch a piece of *wet* red litmus paper with a piece of marble. Result? Support a lump of marble about 5 c.c. in volume on a triangle of iron wire laid upon a ring of the ring stand, and heat the marble ten to fifteen minutes in the hottest Bunsen flame — in a blast-lamp, if possible. When the marble is cold, touch wet, red litmus with the part that was heated. Result? Explain. What products are formed when marble is heated (*cf.* Experiment XLVIII, *b*)?

Slake about 5 c.c. of quicklime by adding to it water, drop by drop, as long as the water is taken up *readily*. Wait for the result, and describe it. Is there a temperature effect? Equation?

b. To a piece of *old* mortar in a test tube add dilute hydrochloric acid. Identify the gas. What does fresh mortar absorb from the air?

c. Stir 10 c.c. plaster of Paris in an evaporating dish with enough water to form a fairly thick paste. Put the paste upon a piece of paper, and push into it a coin slightly coated with vaseline. At once wash the evaporating dish. Let the paste and coin stand an hour or more. Carefully remove the coin from the plaster. Result?

d. To a solution containing a calcium salt, *i. e.*, calcium ions, add *ammonium carbonate* solution. Result? See Experiment LIX, *d.*

e. Clean a platinum wire as in Experiment LIX, *e.*, and determine what color *calcium chloride* gives to the flame. Repeat with *calcium sulphate*. Be sure to have concentrated hydrochloric acid upon the wire.

EXPERIMENT LXIII.

STRONTIUM AND BARIUM.

Apparatus. — Platinum wire and test tubes.

Materials. — Strontium chloride and nitrate, barium chloride and nitrate; solutions of strontium and barium chlorides; ammonium carbonate solution; dilute sulphuric acid.

a. Treat 2 c.c. *strontium chloride* solution with a few drops of ammonium carbonate solution. Result? Repeat, using *barium chloride* in place of strontium chloride. Write equations.

b. Treat 2 c.c. strontium chloride solution with dilute

sulphuric acid. Result? See Experiment XLIV, *a*. Equation?

c. Clean the platinum wire as in Experiment LIX, *e*, and heat a bit of strontium chloride in the flame. Repeat with *strontium nitrate*, $\text{Sr}(\text{NO}_3)_2$. Results?

d. Repeat *c*, using the corresponding barium salts. Results? How distinguish between calcium, strontium, and barium salts?

EXPERIMENT LXIV.

MAGNESIUM.

Apparatus. — Tongs, test tubes.

Materials. — Magnesium wire, dilute hydrochloric acid, solutions of magnesium sulphate and chloride, disodium hydrogen phosphate, and ammonium chloride and hydroxide, magnesite.

a. Hold a piece of magnesium wire 2 cm. long in the flame (use tongs). Result? Describe the product.

b. Treat a second piece of magnesium with dilute hydrochloric acid. Result? Identify the gas, and write the equation. See Experiment X.

c. To 2 c.c. of magnesium sulphate solution add sodium carbonate solution. Result? Repeat, using *magnesium chloride* instead of the sulphate.

d. See Experiment LIV, *d*, for the action of a solution containing a magnesium salt with disodium hydrogen phosphate and ammonium hydroxide. Rewrite the equations here.

Repeat that experiment with *magnesium chloride* solution instead of the sulphate. Equation?

e. Treat a small piece (half a c.c.) of magnesite with dilute nitric acid. Result? Identify the gas, and write the equation.

From Experiment XLVIII, b, tell the effect of heat upon magnesite.

EXPERIMENT LXV.

ZINC.

Apparatus. — File or sand-paper, knife, iron dish with flat bottom, test tubes, mouth blowpipe.

Materials. — Zinc, tin, lead, and copper; zinc dust; solutions of zinc sulphate, sodium hydroxide, and ammonium sulphide; dilute sulphuric and hydrochloric acids; hydrogen sulphide; stick of charcoal.

a. Clean part of a piece of zinc with a file or with sand-paper. Color? Is zinc hard or soft (use a knife or rough edge of glass)? Place a burner below the center of an iron dish. At equal distances from the center place pieces of zinc, tin, lead, and copper, and determine the order in which they *melt*. Return the metals to the proper bottles.

b. Heat a piece of zinc on charcoal with the *oxidizing flame and with the reducing flame* produced by the mouth blowpipe. Results? To do this proceed as follows:—

Hollow out a depression near one end of the charcoal, and into it put the zinc. To make the blowpipe flame, have a *luminous* Bunsen flame 4 cm. high, and hold the blowpipe so that the flame produced will be inclined about 30 degrees to the horizontal plane.

To make an **oxidizing** flame, hold the end of the blowpipe *inside* the luminous flame, a centimeter above the tip of the dark, inner cone. Hold the charcoal at such a distance that the zinc is in the outer, faintly-luminous part of the blowpipe flame.

To make a **reducing** flame, hold the tip of the blowpipe just at the *outer edge* of the flame at its middle part, and hold the *assay* (here, zinc) much nearer the blowpipe than in the oxidizing flame. The proper region is just at the tip of the *inner, light-blue* cone of the blowpipe flame.

c. What action has hydrochloric acid upon zinc? Equation? See Experiment VIII for the action of dilute sulphuric acid, and Experiment XVII for the behavior of *zinc sulphate* crystals, $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$, when heated.

d. Mix 1 c.c. zinc dust with 5 c.c. sodium hydroxide solution, and heat carefully. Test evolved gas with a flame. Result? The solution contains *sodium zincate*, Na_2ZnO_2 . Write the equation.

e. To 2 c.c. zinc sulphate solution add a drop of sodium hydroxide solution. Result? What, probably, is the precipitate? Equation? Repeat with a second test tube. Now add to the first tube dilute hydrochloric acid, shaking. To the second tube add an *excess* of sodium hydroxide, shaking. Results? The alkaline solution contains sodium zincate. Equations?

What do these experiments show as to the nature of zinc hydroxide?

f. To 10 c.c. zinc sulphate solution add a drop of dilute sulphuric acid, and then hydrogen sulphide. Result? Put the solution into a beaker and add 5 c.c. *ammonium sulphide* solution, stirring. Result? The product is *zinc sulphide*, ZnS . Color? Equation?

Add 10 c.c. water, stir the mixture, let it settle, and then pour off the *supernatant* liquid. Add 15 c.c. more water, stir, let settle, and *decant*, i. e., pour off the water. This is called "washing by decantation."

To the zinc sulphide add dilute sulphuric acid. Result? What is the gas? Equation? Why was not zinc sulphide precipitated by hydrogen sulphide?

EXPERIMENT LXVI.

EQUIVALENT OF ZINC.

Apparatus. — Same as in Experiment X.

Materials. — Zinc, in sheet form or in sticks; dilute (5%) sulphuric acid.

a. Dissolve zinc in dilute sulphuric acid just as you did magnesium in Experiment X, and find the volume of hydrogen liberated by a known weight of zinc. Use from 0.45 gram to 0.55 gram of zinc. If the zinc is in sheet form, it will react readily; but a little impurity, chiefly carbon, will remain insoluble. If the zinc is *pure*, it will react with difficulty; therefore wind about the zinc a piece of platinum wire or a narrow strip of platinum foil. Set the apparatus aside until the zinc is in solution; then proceed as in Experiment X.

b. Reduce the volume of hydrogen to *standard conditions*, and calculate the *weight* of the hydrogen obtained. Finally, solve for x in the proportion, —

Wt. of zinc taken : Wt. of hydrogen obtained :: x : 1.

The value of x will be the **equivalent** of zinc.

EXPERIMENT LXVII.

CADMIUM.

Materials. — Cadmium sulphate, hydrogen sulphide, ammonium sulphide.

a. Dissolve completely not more than 1 c.c. *cadmium sulphate*, CdSO_4 in 5 c.c. water, and add hydrogen sulphide *in excess*. Result? The visible product is *cadmium sulphide*, CdS . Color? Equation? What other sulphides of the same color have you had? Wash the precipitate *by decantation*, and treat it with 5 c.c. ammonium sulphide. Result? How distinguish between cadmium sulphide and other sulphides of the same color?

EXPERIMENT LXVIII.

MERCURY.

Apparatus. — Pipette (medicine dropper).

Materials. — Mercury, concentrated nitric acid, hydrogen sulphide, hydrochloric acid, sodium hydroxide and potassium iodide solutions, ammonium hydroxide, zinc, and copper.

Caution. — Before working with mercury remove *all rings*. Do not throw mercury away; but ask what you are to do with it.

a. By means of a pipette take from the mercury bottle a globule three times as large as an ordinary water drop; add to it 2 c.c. water and 2 c.c. concentrated

nitric acid. Result? Let stand until action stops; this may take some hours.

b. While waiting for *a*, dissolve a globule of mercury the size of a water drop in concentrated nitric acid; this gives *mercuric nitrate*, $\text{Hg}(\text{NO}_3)_2$. Equation (cf. Experiment XXXVII, *g*)? Dilute with 15 c.c. water.

c. To 2 c.c. mercuric nitrate solution (*b*) add hydrogen sulphide. Result? The precipitate is *mercuric sulphide*, HgS . Equation?

d. Add to *separate* portions of the nitrate solution, **hydrochloric acid**, **sodium hydroxide** solution, and **potassium iodide** solution, *respectively*. Results? Add the potassium iodide *drop by drop*, noting changes. Write equations where possible.

Note.—With sodium hydroxide we should expect *mercuric hydroxide*, $\text{Hg}(\text{OH})_2$; this, however, decomposes into the *oxide* and *water*.

e. Note the result of *a*. The crystals are *mercurous nitrate*, HgNO_3 ; pour out into a beaker, and add 15 c.c. water and a drop of strong nitric acid.

f. To 2 c.c. of the mercurous nitrate solution of *e* add *hydrogen sulphide*. The precipitate is *mercuric sulphide* and *mercury*. Write the equation.

g. Repeat *d* with the *mercurous* instead of the *mercuric* nitrate. Results? With sodium hydroxide the precipitate is *mercurous oxide*, Hg_2O . Write the equations. Treat the precipitate produced by hydrochloric acid with *ammonium hydroxide*. Result?

h. Into the rest of the mercurous nitrate put a strip of zinc and a copper wire. Results? Now rub them dry. Results?

i. Classify the results of *c*, *d*, *f*, and *g* in five vertical columns.

Formula of Precipitant.	Mercuric Nitrate.		Mercurous Nitrate.	
	Formula of Ppt.	Color.	Formula of Ppt.	Color.
NaOH, etc.				

EXPERIMENT LXIX.

COPPER.

Apparatus. — File or sand-paper.

Materials. — Copper wire, concentrated hydrochloric acid; solutions of cupric sulphate, ammonium hydroxide, sodium hydroxide, and cupric nitrate; grape-sugar; iron nail.

a. File a piece of copper bright. Color? Is it hard or soft? From Experiment LXV give its *fusibility* compared with zinc, etc. By holding one end of the wire in the flame determine if it is a conductor of heat.

b. From Experiments XXXVII and XLII tell the action of nitric and sulphuric acids upon copper. Find out if copper reacts readily with concentrated hydrochloric acid.

c. To 2 c.c. cupric sulphate solution add *ammonium hydroxide* solution in excess. Result? Repeat with *sodium hydroxide* instead of ammonium hydroxide.

Result? Repeat, having the cupric sulphate *hot*, and then add the sodium hydroxide. Result? The last precipitate is *cupric oxide*, CuO . How formed (*cf.* Experiment LXVIII, *d* and *g*)?

d. From Experiment XLI, *b* and *c*, tell the effect of hydrogen sulphide upon cupric sulphate. Equation? Pass hydrogen sulphide into cupric nitrate solution. Result? Equation? What is the effect of heating *blue vitriol* (*cf.* Experiment XVII, *d*)?

e. Dissolve half a c.c. powdered *grape-sugar*, $\text{C}_6\text{H}_{12}\text{O}_6$, in 2 c.c. water, and add it to 5 c.c. cupric sulphate solution. Now add sodium hydroxide solution, shaking until the precipitate first formed is redissolved. Color? Warm carefully, noting changes. Let stand. Results? Color of product? It is *cuprous oxide*, Cu_2O . What effect had the grape-sugar?

f. Put an iron nail into cupric sulphate solution. Result?

EXPERIMENT LXX.

SILVER.

Materials. — Silver foil, silver nitrate solution, nitric acid, sodium thiosulphate; solutions of sodium chloride and potassium bromide, iodide, and cyanide; filter paper; hydrogen sulphide.

a. In a test tube treat a piece of silver foil with 2 c.c. concentrated nitric acid. Result? Equation? Dilute with water to 10 c.c.

b. To 2 c.c. of the solution of *a* add 5 c.c. sodium chloride solution. Result? Equation (*cf.* Experiment

XXII, j)? Boil the contents of the tube. Result? Get the precipitate on filter paper, and expose it to sunlight. Result?

c. To 5 c.c. of solution *a* add 1 c.c. potassium bromide solution. Result? Heat to boiling, pour off the supernatant liquid, and add to half of the precipitate *sodium thiosulphate* solution, $\text{Na}_2\text{S}_2\text{O}_3$ (make this by dissolving the crystals in water). Result? Expose the other half on filter paper to sunlight. Result?

d. To 1 c.c. silver nitrate solution add 1 c.c. *potassium iodide* solution. Result? Equation?

e. To 1 c.c. silver nitrate solution add hydrogen sulphide. Result? Equation?

f. To 1 c.c. silver nitrate solution add *potassium cyanide* solution, drop by drop. Result. Equation? Continue adding it, shaking, until it is in excess. Result? The solution contains the *double cyanide*, $\text{KCN}.\text{AgCN}$, *i. e.*, $\text{KAg}(\text{CN})_2$. Add sodium chloride solution. Result? Explain the result in terms of the ionic theory (*cf.* Experiment XXX).

EXPERIMENT LXXI.

ALUMINUM.

Apparatus. — Test tubes, tongs, blast-lamp.

Materials. — Aluminum wire and filings, white muslin, hydrochloric acid; solutions of sodium hydroxide, aluminum sulphate, sodium carbonate, alum, ammonium hydroxide, and cochineal; powdered alum, sodium bicarbonate, potassium sulphate, ammonium sulphate, aluminum sulphate.

a. Determine whether aluminum is a conductor of heat as in Experiment LXIX, a. Does the wire melt in the Bunsen flame (use tongs)? Try the blast-lamp. Result?

b. To 2 c.c. aluminum filings add 5 c.c. concentrated hydrochloric acid, and warm. Result? Test the gas. Equation?

c. Wash the filings remaining from b, by decantation, add 5 c.c. concentrated sodium hydroxide solution, and warm carefully. Determine the nature of the gas evolved. Result? The solution contains *sodium aluminate*, Na_3AlO_3 (cf. Experiment LXV, d). Equation?

d. To 5 c.c. of *aluminum sulphate* solution, $\text{Al}_2(\text{SO}_4)_3$, add 1 c.c. sodium hydroxide solution. Result? Equation? Get half of the precipitate into a second test tube, and add an excess of sodium hydroxide solution. Result? If the solution now contains sodium aluminate, Na_3AlO_3 , write the equation. To the other half of the precipitate add hydrochloric acid. Result? Equation? Compare with this the behavior of *zinc hydroxide*.

e. Dissolve as much *ammonium sulphate* as possible in 5 c.c. hot water, and add to it in a beaker 5 c.c. water similarly saturated with *aluminum sulphate*. Cool the mixture. Result? The product is *ammonium alum*. Heat again to complete solution, and let stand over night. Result? Shape of crystals?

f. Repeat e, using *potassium sulphate* instead of ammonium sulphate. Results? Compare the crystals.

g. To 5 c.c. of the solution of any aluminum salt add *sodium carbonate* solution. Result? Identify the escaping gas. The precipitate is *aluminum hydroxide*, $\text{Al}(\text{OH})_3$. Mix a cubic centimeter of powdered alum

with a cubic centimeter of sodium bicarbonate, and add water. Result?

h. To 1 c.c. of a solution of cochineal add 5 c.c. alum solution, immerse a piece of white muslin, and then add ammonium hydroxide solution, shaking. Results?

EXPERIMENT LXXII.

IRON.

Apparatus. — Test tubes, tongs, blast-lamp, magnet, beaker.

Materials. — Iron wire and filings, copper wire; hydrochloric, sulphuric, and nitric acids; solutions of potassium ferrocyanide, ferricyanide, and sulphocyanate; ammonia water, hydrogen sulphide, ammonium sulphide, solid ferrous sulphate, and ferric chloride.

a. Compare the heat conductivity of iron wire with that of copper. Test its magnetic properties; its fusibility in the Bunsen flame and the blast-lamp. Results?

b. Treat 3 c.c. iron filings in a beaker with 20 c.c. dilute hydrochloric acid, stirring. Results? Identify the gas. If the solution contains *ferrous chloride*, FeCl_2 , write the equation. When action almost ceases, filter off 10 c.c. of the solution. Color of filtrate?

c. Divide the filtrate of *b* into four parts. To the *first* add a few drops of *potassium ferricyanide* solution, $\text{K}_3\text{Fe}(\text{CN})_6$. Result? This is "*Turnbull's blue*." To the *second* portion add ammonia-water. Result. Equation? Note any change on standing in the air. To the *third* part add *potassium ferrocyanide*, $\text{K}_4\text{Fe}(\text{CN})_6$.

Result? To the last portion add *potassium sulphocyanate* solution, KSCN. Result?

Wash out your test tubes and beakers at once.

d. Filter the remainder of the ferrous chloride solution of b, and add 2 c.c. concentrated nitric acid. Heat carefully for two minutes in a beaker. Resulting color? The solution contains *ferric* chloride and nitrate. To a drop of it in a test tube add a drop of potassium ferricyanide solution; if it still gives a blue precipitate, add 2 c.c. more nitric acid, and boil again.

Treat the resulting substance in *four* test tubes with the reagents used in c. Result in each case?

The precipitate from potassium ferrocyanide and a ferric salt is "**Prussian blue.**"

e. Classify the results of c and d (last part) in five vertical columns.

Formula of Reagent.	Ferrous Chloride.		Ferric Chloride.	
	Precipitate or Solution?	Color.	Precipitate or Solution?	Color.

f. In a test tube shake 2 c.c. powdered *ferrous sulphate* with 10 c.c. water, pour off half of the solution, and pass hydrogen sulphide into it. Result? Does all the iron appear to be precipitated? Write the equation representing the reaction you would expect to take place.

From Experiment XLI tell the effect of dilute sulphuric acid upon ferrous sulphide. Write the equation here. Compare these two equations. Conclusion?

To the other half of the ferrous sulphate solution add five drops of dilute sulphuric acid, and pass in *hydrogen sulphide*. Compare with the result without the acid. Now add *ammonium sulphide*. Result? Equation?

g. Dissolve 1 c.c. *ferric chloride*, FeCl_3 , in 10 c.c. water, and pass in hydrogen sulphide at least *two* minutes. Result? Boil the contents of the tube, and then filter. Test the filtrate with a drop of potassium ferricyanide solution. Result and conclusion?

Determine the nature of the residue on the filter paper by collecting it on a piece of porcelain and igniting it. Odor?

Write the equation for the action of hydrogen sulphide on ferric chloride.

EXPERIMENT LXXIII.

NICKEL AND COBALT.

Apparatus. — Platinum wire, test tubes.

Materials. — Nickel and cobalt and their nitrates; *solutions* of the nitrates; borax, sodium hydroxide solution, concentrated, chemically pure hydrochloric acid.

a. Give the physical properties of cobalt and nickel from an examination of the metals. Effect of a magnet?

b. To 2 c.c. *nickel nitrate* solution, $\text{Ni}(\text{NO}_3)_2$, add a drop of hydrochloric acid and then hydrogen sulphide. Result? Now add *ammonium sulphide*. Result? Equation? Explain the results from Experiments XLI and LXXII, f.

c. Make a borax bead as in Experiment LVIII, *a* and *b*, and determine the color given to it by nickel nitrate.

d. Repeat *b* and *c* with *cobalt nitrate*, $\text{Co}(\text{NO}_3)_2$, instead of nickel nitrate. Results?

e. To 2 c.c. cobalt nitrate solution add sodium hydroxide solution, a drop at a time, until it is in excess. Results?

f. To 2 c.c. cobalt nitrate solution add 5 c.c. concentrated, chemically pure hydrochloric acid. Result? Dilute with water. Result?

EXPERIMENT LXXIV.

MANGANESE COMPOUNDS.

Apparatus. — Platinum wire, test tubes.

Materials. — Manganese sulphate, potassium permanganate, ferrous sulphate, grape-sugar, ammonia-water, hydrogen sulphide, and ammonium sulphide.

a. Dissolve 1 c.c. powdered *manganese sulphate*, MnSO_4 , in 5 c.c. water. To *half* of it add a drop of dilute sulphuric acid and then hydrogen sulphide. Result? Now add *ammonium sulphide*. Result? Color? Equation? Explain the results.

b. To the other half of solution *a* add ammonia-water. Result? Equation?

c. To 2 c.c. ferrous sulphate solution (*cf.* Experiment LXXII, *f*) add potassium permanganate solution. Result? Continue, drop by drop, until the solution is just *faintly* pink. Now add ammonia-water. State and explain the result (*cf.* Experiment XLII, *f*).

d. Dissolve a crystal of *potassium permanganate*, KMnO_4 , in water, and add grape-sugar solution. Result? Explain (cf. Experiment LXIX, e).

e. From Experiment XXI tell the action of *manganese dioxide* with hydrochloric acid; from Experiment V, with *potassium chlorate*; from Experiment LIII, with *hydrogen peroxide*; and from Experiment LVIII, a, tell the color of the *manganese bead*.

EXPERIMENT LXXV.

CHROMIUM COMPOUNDS.

Apparatus. — Chlorine generator, platinum wire, evaporating dish, test tubes.

Materials. — Solutions of potassium chromate and dichromate, of chromic chloride, of potassium and sodium hydroxides; hydrochloric acid, alcohol, borax, barium chloride solution, chrome-alum.

a. What is the color of solutions of *potassium dichromate* ($\text{K}_2\text{Cr}_2\text{O}_7$), *potassium chromate* (K_2CrO_4), and of *chromic chloride* (CrCl_3)?

b. Treat 1 c.c. of *potassium dichromate* solution with a drop of potassium hydroxide solution. Result? From the color tell what is formed.

Complete the equation,



c. To 1 c.c. *potassium chromate* solution add a drop of concentrated hydrochloric acid. Result? What is formed?



How can a dichromate be changed to a chromate?
A chromate to a dichromate?

d. To 2 c.c. potassium chromate solution add barium chloride solution. Result? Equation? Repeat with *chromic chloride* instead of the chromate. Result?

e. To 1 c.c. chromic chloride solution add a drop of sodium hydroxide solution. Result? Equation? Now add the alkali *in excess*, shaking. Result? The solution contains a *chromite*, NaCrO_2 . What other elements behave in this way? See Experiments LXV and LXXI. Save for *g*.

f. Repeat *e* with potassium chromate instead of *chromic chloride*. Result? In what three ways can a chromic salt be distinguished from a chromate?

g. To the clear solution of *e* add *chlorine* gas until there is no further change. Do this in a gas-chamber. Results? Test the resulting solution as in *b*, *c*, and *d*. Results? How can a chromic salt be changed into a chromate?

h. To 10 c.c. potassium dichromate solution in an evaporating dish add 2 c.c. concentrated hydrochloric acid and 2 c.c. ethyl alcohol. Boil until *bright green*, but not to dryness. Test a part of the liquid with barium chloride solution. Result? With potassium hydroxide solution. What does the green solution contain? How can a chromate be changed to a chromic salt? See, also, Experiment XLII, *f*.

i. Refer to Experiment LVIII for the borax bead test. Repeat with a tiny piece of *chrome-alum*. Result?

EXPERIMENT LXXVI.

LEAD.

Apparatus. — File or knife, test tubes, mouth blowpipe.

Materials. — Lead; hydrochloric, nitric, and sulphuric acids; lead nitrate, solutions of potassium chromate and sodium hydroxide, lead oxide, stick of charcoal.

a. File or cut off the coating on lead. Is it hard or soft? Color? Try to mark on paper with lead. Result? Refer to Experiment LXV, *a*, for its fusibility. Treat a small piece with hydrochloric acid, both the dilute and the strong. Results? Wash the lead, and add 2 c.c. concentrated nitric acid and 2 c.c. water. Heat gently. Result? Write the equation (*cf.* Experiment XXXVII).

b. Heat one-fourth of a c.c. of *lead monoxide* on charcoal in the *reducing* flame (mouth blowpipe). See Experiment LXV, *b*. Result? How identify the product?

c. Dissolve 2 c.c. powdered *lead nitrate*, $\text{Pb}(\text{NO}_3)_2$, in 15 c.c. water, heating. Cool, and add to 2 c.c. of the solution 5 c.c. dilute hydrochloric acid. Result? Equation? Wash the precipitate by decantation, and heat it with 10 c.c. water. Result? Cool the solution. Result?

d. To 2 c.c. of the lead nitrate solution add dilute sulphuric acid. Result? Use *potassium chromate* solution instead of sulphuric acid. Result? Equation in each case?

From Experiment XLI, *d*, tell effect of *hydrogen sul-*

phide upon lead nitrate. For the reduction of *lead oxide* by charcoal, see Experiment XLVIII, *a*.

e. To 2 c.c. lead nitrate solution add a drop of *sodium hydroxide* solution. Result? Equation? Now add an excess, shaking. Result? What *three* other hydroxides behave in the same way? See Experiment LXXV, *e*.

f. Put into the remainder of the lead nitrate solution a strip of zinc. Leave it *at least* ten minutes. Result? Equation (*cf.* Experiment LXIX, *f*)?

EXPERIMENT LXXVII.

TIN.

Apparatus. — Test tubes, stopper and delivery tube, mouth blowpipe.

Materials. — Tin (granular and in a bar); concentrated hydrochloric and nitric acids; solutions of mercuric chloride, stannic chloride, and sodium hydroxide; ammonium sulphide, hydrogen sulphide, zinc, sulphur, stick of charcoal.

a. Treat about 2 c.c. of small bits of tin with 10 c.c. concentrated hydrochloric acid in a test tube. Warm gently to start the action, and when the effervescence is vigorous attach a stopper and delivery tube and collect the gas over water. Identify the gas. Result? The solution contains *stannous chloride*, SnCl_2 . Equation? Let the action continue at least ten minutes.

b. From Experiment LXV, *a*, compare the fusibility of tin with that of lead, etc. Hold a bar of tin near your ear, and bend it. Result? What color has bright tin? Is it hard or soft?

c. To 1 c.c. *mercuric chloride* solution, HgCl_2 , add 4 or 5 c.c. of your stannous chloride solution, and then heat. Note all the changes. The solution contains *stannic chloride*, SnCl_4 . Equation?

d. To 2 c.c. stannous chloride solution add 5 c.c. water and then hydrogen sulphide. Result? Color? Equation? Wash the precipitate by decantation, and add 5 c.c. *ammonium sulphide* (use an evaporating dish or beaker) and a small lump of sulphur. Warm gently, and stir. Result? Cool, and add dilute hydrochloric acid in excess. Result? Compare the color with that of the original precipitate.

e. To 2 c.c. stannous chloride solution add 1 c.c. concentrated nitric acid, and heat gently. The solution contains *stannic chloride*. Dilute with 5 c.c. water, and pass in hydrogen sulphide. Result? Color? Stannic sulphide is SnS_2 . Equation? Wash the precipitate by decantation, add ammonium sulphide and a bit of sulphur, and warm gently. Result? Add an excess of dilute hydrochloric acid. Result? Compare with the color of the original precipitate, and with that obtained at the end of d. Conclusion?

f. To 2 c.c. stannic chloride solution add sodium hydroxide solution, drop by drop. Result? Add an excess. Result? What other hydroxides have behaved in the same way? See Experiment LXXVI, e.

g. Pour the solution of a from any unused tin, and put into it a strip of zinc. Result? Equation? Compare with Experiment LXXVI, f.

h. Heat a piece of tin on charcoal in the *oxidizing flame* (mouth blowpipe). See Experiment LXV, b. Results?

EXPERIMENT LXXVIII.

COMPOSITION OF CARBON COMPOUNDS.

Apparatus. — Iron dish (sand bath), test tubes, stopper and delivery tube, ignition tube, rubber connector.

Materials. — Sugar, starch, oxalic acid, benzoic acid, powdered cupric oxide, lime-water, gelatine (powdered), soda-lime, urea, litmus.

a. In an iron dish (sand bath) heat one cubic centimeter of *sugar* as long as a change occurs. Repeat with *starch*; with a crystal of *oxalic acid*. Results? What proof have you that the sugar and starch contain carbon? The oxalic acid?

b. Heat half a c.c. of oxalic acid crystals in a test tube. Determine whether carbon dioxide is evolved or not. Results? Heat half a c.c. of *benzoic acid* in a test tube. Result? Is there any evidence of carbon dioxide?

Recall Experiment XLVIII, a. Repeat it, using one-fourth of a c.c. of benzoic acid and five times its volume of powdered cupric oxide instead of the charcoal and lead oxide. Results? Is there any evidence that hydrogen was present in the benzoic acid? What precaution is necessary to be *certain*, if it is known that the cupric oxide used is slightly hygroscopic?

c. Recall Experiment XXXIII, a. Repeat it, using powdered *gelatine* in place of the glue, and powdered *soda-lime* instead of slaked lime. Results? Repeat it again with *urea* in place of the gelatine. Conclusions? If glue and gelatine represent the class of *albumins*, what element must the members of this class contain?

EXPERIMENT LXXIX.

HYDROCARBONS.

Apparatus. — Mortar and pestle, ignition tube 15 cm. long, ring stand, clamp, delivery tube, rubber connector, test tubes, 100 c.c. flask, wire gauze, one-hole stopper, pneumatic trough, evaporating dish.

Materials. — Dry soda-lime and fused sodium acetate, lime-water, bromine water, concentrated sulphuric acid, "95 per cent" ethyl alcohol, calcium carbide, benzene.

a. Methane. — In a mortar powder and mix 2 grams of soda-lime and 1 gram of dry, fused sodium acetate. With the mixture half fill an ignition tube 15 cm. long, and attach a delivery tube by means of a rubber connector. Support the tube horizontally, tap it to insure a passage for gas, and heat it with a moving flame. Collect the evolved gas — it is impure methane (*cf.* § 292) — in three test tubes. Note its physical properties and combustibility. After burning a test tube of the gas, pour lime-water into the tube, close it with the thumb, and shake it. Result? Conclusion? To one test tube of methane add a drop of bromine water. Close the tube, and shake it. Does the color of the bromine disappear?

b. Ethylene. — In a 100 c.c. flask *cautiously* add 10 c.c. of concentrated sulphuric acid to 5 c.c. of alcohol. Shake the flask after each addition of acid so as to insure mixing. Support the flask *over* wire gauze but not quite touching it, and attach a stopper and a delivery tube with a rubber connector. *Do not leave the delivery tube in the*

water when you stop heating! Heat with a small flame until a regular stream of gas comes off, and collect three test tubes full over water. Note its physical properties and the character of its flame. Test with lime-water and bromine water as in *a*. Results?

c. Acetylene. — In a test tube mix 2 c.c. — *no more* — of water with 5 c.c. of alcohol. Add two pieces of *calcium carbide* the size of peas, and at once attach a stopper and delivery tube. Collect the evolved gas (acetylene) over water in three test tubes. Note its properties as directed in *a* and *b*. *Do not inhale it.*

d. Benzene. — Put half a cubic centimeter — *no more* — of *benzene*, C_6H_6 , in an evaporating dish. Note its odor. Carefully ignite the benzene. Describe its flame. Write the equation for the combustion of benzene, if the products are carbon dioxide and water.

EXPERIMENT LXXX.

ETHYL ALCOHOL.

Apparatus. — Flask (100 c.c.), stopper and delivery tube, test tubes, evaporating dish, distilling apparatus.

Materials. — Molasses (or powdered grape sugar), yeast, lime-water (or baryta water), litmus, sodium bicarbonate, alcohol, powdered shellac or rosin.

a. To 25 c.c. water in a 100 c.c. flask add 5 c.c. molasses or powdered grape sugar and about one cubic centimeter of compressed yeast. Attach tightly a stopper with a delivery tube, and let the tube pass into 5 c.c. lime-water or baryta water in a test tube. Let the

flask stand in a warm place, and note results. If you leave the delivery tube in the lime-water over night, see that it dips only slightly below the upper surface of the liquid. Why? If the test tube contains no precipitate the next day, heat its contents to boiling. Explain the result. Test the reaction of the solution in the flask toward litmus. Result?

b. Ask the teacher to collect from several students the dilute alcohol they have prepared, and to distill it, if this was not done in connection with § 280. If the first portions of the distillate do not burn when a flame is applied they must be *redistilled*. The first few drops may then be tested for alcohol.

c. Set some of the fermented solution aside, without stoppering the flask, for a week or two. Then note the taste of the solution, its reaction to litmus and its effect upon a little solid sodium bicarbonate in a test tube. Results?

d. Put two or three drops of alcohol into an evaporating dish, warm the dish slightly, and apply a flame. Note the color of the alcohol flame. Write the equation for its combustion.

e. Treat half a cubic centimeter of powdered shellac or rosin in a test tube, with 5 c.c. alcohol. Close the tube with the thumb, and shake it. Result? Add 5 c.c. water. Result? Let the tube stand until the next period. Result?

EXPERIMENT LXXXI.

ETHYL ETHER.

Apparatus. — Evaporating dish, test tubes.

Materials. — Ethyl ether, paraffin.

Caution. — *Do not bring the bottle of ether near a flame!*

a. Put two drops of ether into an evaporating dish, remove the ether bottle, and apply a flame to the ether in the evaporating dish. Describe the flame.

b. In a test tube add 2 c.c. ether to a piece of paraffin half the size of a pea, shaking. Result? Pour the ether out into the evaporating dish, and hold the dish in the hand to drive off the ether. Result? Note the volatility and odor of the ether.

EXPERIMENT LXXXII.

ALDEHYDES.

Apparatus. — Test tubes, stirring rod, ring stand or rack, tongs.

Materials. — Granular potassium dichromate, concentrated sulphuric acid, methyl alcohol, ethyl alcohol; solutions of silver nitrate, caustic soda, and ammonia; copper wire for spiral.

a. In a test tube add 2 c.c. of concentrated sulphuric acid to 6 c.c. of water, cool the mixture under the tap, and add 2 c.c. of alcohol. Pour this mixture upon 2 c.c. of granular potassium dichromate in a test tube.

Hold the test tube over the sink. Results? Note the odor of the escaping vapors of *acetaldehyde*, CH_3CHO . Hold in the vapors a stirring rod wet with *ammoniacal* silver nitrate solution. To make this, add one drop of a 10 per cent solution of caustic soda to 1 c.c. of silver nitrate solution, and then add 1 c.c. of ammonia water. The deposit on the rod is silver. Explain.

b. Put 2 c.c. of *methyl alcohol*, CH_3OH , in a test tube supported in a ring stand or rack. Make a copper spiral by winding about a glass rod or a pencil a foot of copper wire. Remove the pencil or rod, and hold the spiral in the flame (use tongs) until it is red hot. Then drop it into the methyl alcohol. Note the sharp vapor of *formaldehyde*, CH_2O , mixed with the vapor of the alcohol.



EXPERIMENT LXXXIII.

ACETIC ACID AND ACETATES.

Apparatus. — Beaker (50 c.c.), test tubes, evaporating dish, stirring rod, wire gauze, ring stand.

Materials. — Commercial (concentrated and dilute) acetic acid, concentrated sulphuric acid, vinegar, sodium carbonate, litmus and filter papers, alcohol.

a. Note the taste of a drop of *dilute* acetic acid. Heat some to boiling in a test tube. Odor? Its action to litmus? Cf. Experiment XXIV, a and b. Test vinegar in the same ways. Results?

b. In a test tube mix 1 c.c. of concentrated acetic acid with 2 c.c. of alcohol, and add half a c.c. of concen-

trated sulphuric acid. Heat carefully, and describe the odor. It is that of *ethyl acetate*, $\text{CH}_3\text{COOC}_2\text{H}_5$. The sulphuric acid removes water. Equation? If you were given a liquid suspected of being acetic acid, how would you prove it to be this substance?

c. In a 50 c.c. beaker dissolve 10 grams of sodium carbonate in 10 c.c. of water and add to it commercial acetic acid (5 c.c., or less, at a time) until the reaction is distinctly acid on stirring, and effervescence ceases. Then transfer the solution to an evaporating dish, and concentrate it over the wire gauze until a drop held on a stirring rod crystallizes when cool (*cf.* Experiment XXXVII, *g*). Set the dish aside until the next period. Name the crystals. Their shape? Filter them off, and dry them between filter papers.

d. Carefully heat some of the crystals of *c* in a test tube. Do they contain crystal water (*cf.* Experiment XVII)? Treat 1 c.c. of them, in a test tube, with 1 c.c. of concentrated sulphuric acid, and warm gently. Result? Odor? Remember to pour the concentrated acid *into* water when cleaning the test tube!

To 1 c.c. of the crystals add 1 c.c. alcohol and half a c.c. of concentrated sulphuric acid. Warm gently, and note the odor of the vapors. Result? Conclusion?

EXPERIMENT LXXXIV.

OTHER ORGANIC ACIDS.

Materials. — Citric acid, lemon juice, oxalic acid, benzoic acid, alcohol, sodium bicarbonate, potassium permanganate solution, dilute and concentrated sulphuric acid, litmus.

a. For the properties of *tartaric acid* see Experiments XXIV, c; XLVII, a; LX, c; and LXI, b and c.

b. Make an aqueous solution (by heating) of 1 gram, or less, of crystallized *citric acid*, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 + \text{H}_2\text{O}$, and note its taste, odor, and reaction toward litmus and toward sodium bicarbonate. Repeat, using *lemon juice* instead of citric acid solution. Results?

c. See Experiment LXXVIII for the behavior of *oxalic acid*, $\text{H}_2\text{C}_2\text{O}_4$, when heated. Prove the presence of crystal water in oxalic acid. To 1 c.c. of potassium permanganate solution add half a c.c. of dilute sulphuric acid and then oxalic acid solution, drop by drop. Result? Conclusion?

d. Heat 1 c.c. of *benzoic acid*, $\text{C}_6\text{H}_5\text{COOH}$, with 5 c.c. of water. Result? Boil for a moment. Odor of vapors? Now cool the solution under the faucet. Result? Redissolve the benzoic acid by applying heat. Cautiously taste a drop of the solution, and note its action toward litmus and sodium bicarbonate. Results?

In a test tube heat carefully 1 c.c. of benzoic acid with 1 c.c. of alcohol until you get a solution; then add half a c.c. of concentrated sulphuric acid and heat again. Note the odor of the vapors of *ethyl benzoate*, $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$. Pour the solution into 10 c.c. water, and note the separation of the oily ester.

EXPERIMENT LXXXV.

SOAP.

Apparatus. — “Tin” can, stirring rod, test tubes, ring stand.

Materials. — Sodium hydroxide, lard, fine salt, "Castile" or "Ivory" soap, litmus, dilute sulphuric acid, calcium sulphate solution.

a. In a clean "tin" can dissolve 8 grams of sodium hydroxide in 60 c.c. cold water. If possible have the cover only partially cut out, so that it may be pushed down as a lid during the boiling. To the alkaline solution add 25 grams of lard, and heat the mixture to boiling, having the opening of the can almost closed by the lid. *Be careful not to let the alkali spatter into your eyes!*

After thirty minutes *stop the boiling*, and see if the mixture begins to become solid. (Care!) If not, continue heating until it does.

Now add to the mixture, while it is still warm, 16 grams of fine salt in lots of about 2 grams each. Stir *carefully* after each addition. Finally, boil the mixture for ten minutes, and let it cool. The soap will appear as a solid cake on the surface of the solution. Remove it, rinse it with a little water, and let it dry.

b. Dissolve about 1 c.c. of "Ivory" or "Castile" soap in 10 c.c. of water, and test the reaction of the solution with litmus. Result? Treat half of the solution with dilute sulphuric acid. Result? The solid product is a mixture of the organic acids of the soap.

Treat the other half of the soap solution with a solution of calcium sulphate. Result? Heat to boiling. The product is the calcium salt of the acids ("lime soap"). (*Cf.* §§ 70, 413, and 435 of text.)

EXPERIMENT LXXXVI.

CARBOHYDRATES.

Apparatus. — Beaker, test tubes, ring stand, wire gauze.

Materials. — Fehling's solution (see *a*), grape sugar, cane sugar, molasses, concentrated hydrochloric acid, sodium carbonate, starch or starch paste.

a. See Experiment LXIX for the action of grape sugar with alkaline cupric salts. A better solution for testing the sugars is the one called "**Fehling's Solution.**" Cupric sulphate crystals (34.64 grams) and 1 c.c. dilute sulphuric acid are dissolved in water, and the solution is diluted to exactly 500 c.c. This is solution I. Solution II consists of 175 grams of sodium potassium tartrate, 50 grams of sodium hydroxide, and enough water to make the volume exactly 500 c.c. These solutions are kept in separate, rubber-stoppered bottles. Equal volumes of the two are mixed just before they are used. One cubic centimeter of Fehling's solution is completely reduced by exactly 0.005 gram of grape sugar.

To 10 c.c. Fehling's solution in a beaker add a drop of a solution of grape sugar, and heat to boiling over the wire gauze. Result? Let the precipitate settle, and add another drop of grape sugar solution; repeat the process until the Fehling's solution has just lost its blue color. Calculate how much grape sugar you added.

b. In a test tube add some cane sugar solution to 5 c.c. Fehling's solution, and heat to boiling. Is there reduction? Try a solution of molasses instead of cane sugar. Result?

c. To 20 c.c. cane sugar solution in a beaker add 2 c.c. of concentrated hydrochloric acid, and heat gently to boiling for fifteen minutes over the wire gauze. Cool, and neutralize the acid with solid sodium carbonate; then test with Fehling's solution. Result?

d. Repeat *b* and *c*, using 20 c.c. starch solution (make it as in Experiment LI, *d*) instead of cane sugar. Results?

EXPERIMENT LXXXVII.

SOME PRINCIPLES OF QUALITATIVE ANALYSIS.

Apparatus. — Funnel, funnel support, beaker, test tubes.

Materials. — Solutions of nitrates of iron (ferric), silver, copper, barium, and sodium; hydrochloric acid, hydrogen sulphide, dilute sulphuric acid, ammonia water, filter papers, and two or more "unknown" substances.

a. Qualitative Analysis is a system of experiments for the separation and identification of the elements present in mixtures of substances. In a limited sense the term is applied to the detection of the ordinary metals and acids. The separation of metals present as *ions* in a solution is possible if we can convert some of the metals into insoluble compounds while leaving the others in solution. The following experiments show how a scheme of analysis may be devised for the separation of the five metals: *silver, copper, iron, barium, and sodium*. We use solutions of the *nitrates*, since these are all soluble. Make *ferric nitrate*, if this is not found in the laboratory, by covering about 1 gram of iron wire or filings with 10 c.c. of water in a beaker and adding 10

c.c. dilute nitric acid in small portions. When action ceases, filter the solution and dilute it to 60 c.c.

b. To 5 c.c. of each of the nitrates named in *a* add dilute *hydrochloric acid* — one cubic centimeter at a time — until there is an *excess*. To know if you have an excess of the precipitant let the precipitate settle, and add a drop more of the precipitant to the clear solution; or filter a little of the precipitated solution and test the filtrate in the same way. (Cf. § 246, *last two paragraphs*.) Be sure that your test tubes are clean for every test.

Copy the following table in your note book, and put down the results in their places.

Effect of	AgNO ₃	Cu(NO ₃) ₂	Fe(NO ₃) ₃	Ba(NO ₃) ₂	NaNO ₃
HCl					
H ₂ S					
H ₂ SO ₄					
NH ₄ OH					

c. Treat 5 c.c. of each of the solutions named in *a* with hydrogen sulphide in excess. Make sure you have an excess, as suggested in *b*. Tabulate your results. Be sure the tube delivering the gas is clean before every test. For the action of hydrogen sulphide with ferric salts, cf. Experiment LXXII, *g*. For the conversion of *ferrous* ions into the *ferric* state, see Experiment LXXII, *d*.

- *d*. Treat 5 c.c. of each of the five solutions with an excess of dilute sulphuric acid, and tabulate the results.

e. Repeat *d*, using ammonium hydroxide solution in place of sulphuric acid.

f. From the results tabulated in *b* to *e* devise a plan for identifying any one of the five nitrates, and of separating them, if they are all present in a mixture.

g. From previous experiments tell how you would determine whether a white, soluble solid given you was sodium *chlorate*, *nitrate*, *sulphate*, *carbonate*, *sulphite*, *acetate*, or *thiosulphate*?

h. If you wished to make a mixture of copper and barium salts, would you use copper *sulphate*? Why? Why not use barium *chloride* or ferric *chloride* solution if you wish to get a soluble mixture of the ions of these metals and those of silver?

i. Get from the teacher two or more unknown substances, and determine what metal or metals of the five named are present; also what acid.

end

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